

## IRON CORROSION



# IRON CORROSION

ANTI-FOULING

AND

ANTI-CORROSIVE PAINTS

BY

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## PREFACE.

IRON is now used on such a large scale for constructional, industrial, and household purposes, and the difficulties of keeping it bright and free from rust, or coating it in such a way that decay is prevented are so well known that a book on the subject should need but little introduction. In the present work the author has endeavoured to give a fairly complete account of our present knowledge on the subject of the rusting of iron, quoting several authorities. The methods of protecting iron from rusting are next touched upon, including a description of the pigments and oils employed in the manufacture of the paints, and the best methods of compounding these to obtain the desired results. Paint-making machinery is figured and described. A chapter is devoted to the composition of various proprietary protective paints; an abstract of the most important British patents for paints for iron, steel, etc.; and for anti-fouling compositions for ships' bottoms is also included.

The author hopes that those who are interested in this subject may find something in this book which will prove instructive or useful to them.

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## INTRODUCTION.

SINCE the introduction of iron, and especially from the time of its application to industrial and constructional purposes, the need of some material which can be readily applied to it and which will effectively prevent its oxidation or rusting has long been felt.

Iron only rarely occurs in a natural state as a mineral; it is found in certain igneous rocks in Scandinavia in the form of fine particles and also in what are known as meteorites or aerolites in various parts of the world; in the latter case it is alloyed with nickel.

The iron ores are: the oxides, magnetite or magnetic iron ore ( $\text{Fe}_3\text{O}_4$ ), and red hematite ( $\text{Fe}_2\text{O}_3$ ). Brown hematite is a hydrated oxide of iron ( $\text{Fe}_2\text{O}_3 \cdot \text{Fe}_2(\text{OH})_6$ ), ochre and umber being impure varieties, clay ironstone or impure carbonate of iron ( $\text{FeCO}_3$ ) and iron pyrites ( $\text{FeS}_2$ ). In the smelting of iron any of the above ores except iron pyrites are heated together with coal and limestone in a blast furnace with the production of what is known as pig or

cast iron. This is not pure iron but contains more or less carbon (combined and as graphite), sulphur, phosphorus, and silicon. From this pig iron, and also direct from the ores, are obtained in various ways purer forms of iron known as wrought iron and steel. Although pure iron is never used in industry, wrought iron comes nearest to this description as it contains only traces of carbon and the other elements above mentioned. Steel contains a definite amount of carbon entirely combined as a carbide which renders it more or less hard and less fusible and imparts to it the property of being tempered.

The three varieties of iron: cast iron, wrought iron, and steel therefore differ only in minor details from each other, iron being the predominant element in all. On exposure to the atmosphere and moisture they all tend to rust although in varying degrees, cast iron most easily and steel usually with more difficulty, but the rapidity of rusting is influenced very materially according to the condition of the surface of the metal, rusting taking place more readily when the surface is rough or matted than when it is smooth or burnished.

Certain alloys of iron, that is with small quantities of nickel, chromium, tungsten, titanium, and molybdenum, are now very largely employed in the form of steel or cast iron for certain purposes—i.e. for armour plates, guns, tools, and parts of machines—owing to their great hardness or toughness, and

in some cases by reason of their durability. Some of these alloys are quite immune to rusting even without any protective coating or special treatment; they are also unaffected by weak acids, and are for this reason specially useful for chemical plant and household cutlery.



# IRON-CORROSION.

## CHAPTER I.

### IRON RUST AND ITS FORMATION.

THE inorganic and organic materials employed by man, including the metals iron, lead, copper, zinc, etc., and also the noble metals gold and silver, all of which are extensively used in the industrial arts, being subjected to atmospheric influences, consequently the surface of the various utensils into which these metals are formed undergoes alteration. The least susceptible to these influences are gold, silver, and platinum, which metals merely become dimmed on the surface being restored to their original brightness when simply rubbed over thoroughly with a leather or cloth, provided no other agency has affected them, *e.g.*, sulphur or sulphuretted hydrogen in the case of silver. On the other hand, the baser metals such as iron, copper, lead, zinc, etc., under the influence of atmospheric oxygen, carbonic acid and other agencies, acquire a superficial coating, consisting of a combination of the metal with oxygen or carbonic acid, which alters the appearance of the metal, thereby rendering it lustreless and dull. The highly lustrous metal lead becomes coated with a dull grey sheet of oxide; zinc is covered with a dim grey film. Copper turns reddish-brown and subsequently green, becoming coated with the green mould—*æruugo nobilis, patina*—which distinguishes ancient monuments and memorials from those of modern times. This

mould was formed by the action of a pure atmosphere—un-impregnated with the fumes of coal—and, like the thin film of oxide on lead and zinc, it constitutes a protective coating against the further encroachments of the air, since it neither increases in extent beneath nor develops further externally. Objects covered with this layer of oxide withstand for centuries the destructive influence of rain, snow, and changes of temperature, besides which they are also moderately insusceptible to the action of weak acids.

On the other hand, iron, the metal most extensively used at the present day—by reason of its valuable properties and its abundance—is much more susceptible to atmospheric agencies but acquires no protective coat. If a bright piece of iron be exposed for even only a few minutes to the action of water and the latter is allowed to evaporate at a moderate temperature, the clean metal becomes covered with a coherent red coating, which can be easily rubbed off again when dry, but does not leave the surface of the iron in its original condition. Under the agency of the atmosphere and the water a combination of iron and oxygen—iron rust—is formed and the iron is said to be “rusted”. This oxidation occurs on bright surfaces of the metal, such as polished iron or steel, as well as on cast iron or sheet iron; it is observable on all iron objects, large or small, rough or smooth, and will inevitably be produced unless the iron is protected by a suitable protective covering.

Moreover, rust is formed not only on iron articles exposed to the influence of atmospheric air and moisture, but also on iron set in brickwork, or under water, or in the ground and so forth; in fact the action goes on everywhere and is the result of various causes, although water (moisture) is always necessary and in fact the principal rust-forming agency. Iron girders enclosed or embedded in or between layers of brickwork or masonry, iron structures or pipes laid under-

## IRON-CORROSION AND ANTI-CORROSIVE PAINTS.

ground or in water, all rust, and under certain circumstances the layers of rust may attain considerable proportions. Everything made of iron or steel is liable to oxidation. Things carried in the pocket which are kept bright by mutual friction will become rusty when exposed to moisture, a damp place being often sufficient cause; pocket knives become oxidized in the pocket, if not in regular use, and table knives are similarly affected if not cleaned and polished regularly. Nails driven into boxes or other woodwork are rusted by the moisture in the wood; in fact all the numerous things daily employed by man become more or less rusty, whether in use or lying by, and thereby deteriorate both in outward appearance and strength. Iron stove pipes and flues are speedily rusted by the action of gaseous acids formed during the combustion of the fuel, and after prolonged use become gradually converted entirely into layers of rust, so that they either fall to pieces spontaneously or can be broken with ease.

Wherever rust has once formed, its further accumulation is a natural sequence; the prevention of further action therefore becomes impossible by any known means unless the affected places are freed entirely from all traces of the oxide. Rust, far from being a solid, coherent mass, is loose and porous, absorbing and persistently retaining water, which with the conjunction of atmospheric air, assists in the conversion of such portions of the iron as have hitherto remained intact. This is the reason why sheet iron, under conditions favouring rust formation, is finally converted entirely into rust, and though retaining its original form no longer consists of iron but of a compound which easily breaks into pieces under very slight pressure. To this continuous development of rust is also due the complete destruction of rivets and screws in iron structures, and the circumstance that iron pipes of considerable thickness laid

the earth are in course of time entirely converted into rust, breaking in pieces or crumbling away when disturbed.

The thicker the substance of the iron, the longer it takes for the rust to corrode it sufficiently to impair the strength of the article. For example, if a piece of ordinary sheet iron 1 mm. ( $\frac{1}{32}$  in.), and a bar of cast iron 5 to 6 mm. (about  $\frac{1}{4}$  in.) be left to rust under identical conditions, the former will be entirely converted into oxide long before any diminution of strength can be detected in the latter. The cast iron will have acquired a thick coating of rust but still having a considerable core of metal, probably the usefulness of the bar is *apparently* undiminished. Nevertheless as a matter of fact it has really suffered depreciation; since a mass of iron originally 5 to 6 mm. thick, but covered on each side with a 1 mm. layer of rust, having therefore lost altogether 2 mm. of its substance, cannot possibly have retained its primary strength. Moreover, in addition to attacking the surface, the rust, as the result of imperfections in the material, may have penetrated, in places, right through the mass of the metal, and consequently diminished considerably its powers of resistance. Hence in the case of the thicker cast iron the progress of rusting is apparently more gradual than in the thinner sheet metal; its extent, however, may be the same or even greater.

Rust is everywhere formed where moisture and atmospheric air come together; it is visible on the shafting and other parts of machinery, etc., in large workshops, and on water wheels that are not continually under water. It develops on iron firearms when carried during wet or even merely damp weather; also in the interior of the barrel when the weapon is discharged, in consequence of the hygroscopic character of the residual compounds left therein from the combustion of the powder. All hygroscopic salts, especially sodium chloride (common salt) and the chlorides of potassium, magnesium, and calcium, facilitate the formation of rust

when acting in conjunction with atmospheric air; whereas caustic alkalis dissolved in water have no injurious effect on iron provided it remains immersed in the solution. If, however, pieces of iron be stored above solutions of the alkalis, or partly immersed therein, leaving one end projecting, then rust will make its appearance in quantity. Dilute acids are the most active assistants in the development of rust, even such weak organic acids as malic acid being capable of rusting iron or steel in a very short time. Pieces of iron embedded in the earth soon become rusted, the rapidity of the action being in direct ratio to the amount of rust-favouring constituents present. Thus, iron (gas and water) pipes laid below the level of the streets in towns, and especially when the pavement consists of a permeable material—such, for example, as granite setts embedded in sand—rusts much quicker than if situated in arable soil, since they are exposed to the action of the salts contained in the urine of horses and in street mud. Iron in the neighbourhood of manure heaps, or stall-drainage pits, rusts quicker than that in or upon ordinary earth, since the salts of ammonia, etc., formed in such deposits contribute to the production of rust. It has been assumed that iron embedded in earth becomes covered with a protective coating of silicate or carbonate, but this has not yet been definitely proved. It is evident that the formation of such compounds would depend on the character of the soil, *i.e.*, whether there exists ready-formed a sufficiency of silicates or carbonates in a form suitable for action upon the metal before such combination could take place.

We may consider as *rust formers* the following :—

1. Atmospheric air or oxygen.
2. Water—in the form of rain, snow, water of condensation (*e.g.*, dew), and mere moisture, the latter including the moisture in the atmosphere and incipient condensation.

3. All organic and inorganic acids, even the weakest.

4. All chlorine compounds of the metals, alkalis, and alkaline earths, and all salts rich in, or absorptive of, water.

The process of rust formation has until recently received very little attention from the scientific point of view; at least there is little to be found on the subject in accessible sources of information. In practice, however, the conditions—or rather influences—under which rust is developed are well known, and sufficient knowledge of its progress has been gained to justify the axiom that when rust has attained a certain degree of development to arrest its further progress becomes impossible, all the means at our disposal being un-availing.

It is generally assumed that—apart from such chemical agents as acids and salts—water and oxygen are the primary causes of rust, a certain contributory influence being, however, ascribed to atmospheric carbon dioxide (carbonic acid). It may be of interest to quote here the views which have been expressed by eminent chemists as to the mechanism of the formation of rust.

Spennrath says:—

“Chemical analysis shows us that rust is a hydrated oxide of iron, a compound of the metal iron with oxygen and water, 100 parts of dry iron rust containing 52·3 of iron, 22·4 of oxygen, and 25·7 of water. The water is here—and this should be carefully noted—in a state of chemical combination, and not present as a mere mechanical adjunct in the form of moisture. It is therefore by no means contradictory to speak of *dry* iron rust as containing 25 per cent. of *water*. Iron rust being, then, a compound of iron, oxygen, and water, it follows that iron can rust only when and where it is brought into contact with oxygen and water, and that if one of these two essentials is lacking, the formation of rust becomes impossible, and the iron will remain unattacked.

Consequently, iron exposed to the air cannot rust in the absence of water, and iron immersed in water must remain free from rust if access of oxygen is debarred. These statements are proved by facts. Thus, for example, if iron or steel articles are stored over calcium chloride in an enclosed space, they will remain free from rust for an indefinite period, owing to the absorption, by the calcium chloride, of every trace of water in the air of the chamber, and the incapacity of oxygen by itself to attack iron at the ordinary temperature. In this manner a convenient method of protecting surgical or other fine steel instruments from rust is afforded, in that a vessel—preferably of glass—closed by an air-tight lid is employed, on the bottom of which is strewn a layer of calcium chloride, whilst the instruments, etc., to be stored are placed on a perforated false bottom made of cardboard or wood. It is advisable to dip the instruments in strong alcohol, to free them from all adherent traces of moisture, before putting them into the case.

“Steam boilers, when out of use, can be prevented from rusting on the inside by placing trays, containing calcium chloride, in the interior, and then making the boiler air-tight. In this case also the calcium chloride abstracts the moisture from the air, and renders the latter incapable of forming rust.

“If iron be laid in ordinary spring, well, or rain water, it soon gets rusty. If, however, the water has been previously boiled for some time and allowed to cool with exclusion of air, then no rusting occurs, the oxygen present in the water having, like any other gas, been driven off during the boiling, leaving the water free from air; and, provided care be taken to prevent any subsequent absorption of oxygen by the water, iron stored therein will keep free from rust. This explains why boilers do not rust on the inside while in use, the continuous boiling of the water driving out the oxygen

present in solution. Since, however, the feed water is continually introducing fresh quantities of air into the boiler, it follows that the steam chest of the boiler always contains small quantities of oxygen in association with the steam, and hence it comes that rust may form at the water line. The upper layer of water, being in direct contact with the recently liberated oxygen, tends to re-dissolve the same, and thereby to act as a rust former. It will also be noticed that the iron hot-water pipes of heating installations do not rust internally, the water circulating through the pipes having been freed from air and oxygen by the continuous application of heat.

*"The rust-forming agency is a solution of oxygen in water* This constitutes the whole secret of the production of rust. 1,000 parts of water at a temperature of  $0^{\circ}$  C. can take up 49 parts of oxygen gas into solution; but as the temperature rises, the solvent power of the water for this gas, as for all others, decreases, so that at  $10^{\circ}$  C. only 38 parts are dissolved per 1,000; at  $21^{\circ}$  C. only 31 parts; at  $50^{\circ}$  C. only 21 parts, and so on.

"The effective rust-producing energy of the water increases in direct ratio with the amount of oxygen present in solution. Hence it follows that, other conditions being equal, cold water must be more active than hot in this respect; and this also explains a circumstance that probably every one has observed, *viz.*, that iron rusts much more strongly when the contact with water is only intermittent than in cases of permanent immersion. A piece of iron, one end of which dips into fluctuating water, leaving the other projecting into the air, will exhibit the most pronounced area of rust at the part between the extremes of the alteration in the water level. Moreover, a short shower of rain causes a greater formation of rust on iron than would a whole day's complete immersion in water.



“The elucidation of these phenomena is very simple. The thin stratum of water left adherent when iron is wetted is in constant contact with the air and is therefore always saturated with oxygen, that consumed in the formation of rust being immediately replaced from the atmosphere. On the other hand, deeper layers of water do not become saturated with oxygen, and the loss cannot be so quickly made good; whereas raindrops, again, have had the opportunity to absorb, in their fall, the maximum quantity of air they can take up, and consequently when they come in contact with iron constitute actually a saturated solution of oxygen.

“Iron articles stored in a room regarded as ‘dry,’ in the ordinary sense, do not rust. If, however, a closed, airtight case with a little water in the bottom be placed in such a room, and the iron articles be placed in the case without coming into contact with the water, they will be found to have rusted considerably within a very short time.

“This difference in behaviour is highly instructive, though easy of explanation. The air of a living or workroom, like everywhere else, contains water. Here, however, the water is in the gaseous form of water vapour, which is incapable of forming rust even when mixed with oxygen. In the closed case, on the other hand, the air becomes rapidly saturated with water vapour, taking up as much as it can hold at the prevailing temperature; consequently, on the slightest reduction of the temperature a deposition of liquid water takes place on the walls of the case and on the iron articles contained therein, and as this water at the same time absorbs oxygen from the surrounding air the possibility and obligation of the formation of rust is attained.

“Generally the air of a room is in a condition far removed from saturation with water vapour, consequently a considerable fall in temperature would be necessary for attaining the dew-point of such air, with its concomitant deposition of

liquid moisture, and so long as this point is not reached the formation of rust is impossible

“ The opinion extensively prevails that the carbon dioxide present in the air plays an active part in the formation of rust, and it has even been asserted that the action of this oxide is an essential factor in the process. As a matter of fact this view is erroneous. In the first place, gaseous carbon dioxide is of itself quite inert towards iron. Water containing the gas in solution is, however, capable of attacking iron, forming iron carbonate which decomposes—as may have been noticed many times in the case of ferruginous waters—in contact with air, ferric hydrate, *i.e.*, rust, being then formed. That carbon dioxide is not essential to the formation of rust is evidenced by the fact that iron plates stored, in closed vessels, above the surface of water containing in solution caustic potash, caustic soda, or slaked lime, exhibit in every case extensive incrustations of rust. As solutions of the aforesaid caustic alkalis, *e.g.*, caustic potash, are endowed with a great affinity for carbon dioxide, it is therefore clear that the air in such vessels must very soon be entirely freed from that gas

“ A behaviour similar to that of an aqueous solution of carbon dioxide, but generally more strongly developed, is exhibited by other dilute acids in presence of iron. So long as the metal remains in the dilute acid liquid it will be dissolved thereby and the corresponding iron salt will continue to be formed; but when the oxygen of the air is concurrently admitted the case is altered. If metallic iron be moistened with any dilute acid and then exposed to the air a thick coating of rust will very quickly form; and this explains why it is necessary, in cleaning rusty iron by the aid of dilute sulphuric acid, to place the iron in lime water immediately on removing it from the acid-bath, in order to prevent an immediate renewal of the rusting. The action of the lime

water is to neutralise the acid and render it inert. Moreover, the solutions of various salts, especially the chlorine compounds, exert a rusting influence similar to that of the dilute acids. Solutions of common salt, sal ammoniac, magnesium chloride, etc., in particular, are regarded as highly active rust formers. It is true that these compounds favour the development of rust, but, nevertheless, even here the admission of oxygen is a *sine qua non*. That the presence of dissolved salts is no bar to the absorption of oxygen by water can be seen best in sea water, which contains an average of 3·5 per cent. of the above-named salts, without the dissolved oxygen being any smaller in quantity than in fresh water. Indeed, were it not for this solubility of oxygen in sea water the existence of marine animals would be an impossibility.

“The action of rust-forming salts on iron is thus similar to that of dilute acids. In any event the production of rust can only ensue when water and oxygen are both present and active simultaneously.”

Simon expresses himself as follows with regard to the *Origin of Rust*:—

“For rust to be formed it is—under ordinary atmospheric influences—a necessity for the surface of the metal to be exposed, and that water in the liquid condition—containing dissolved oxygen (air) and carbon dioxide—should act thereon. When these factors are not concurrently in action, no formation of rust takes place so long as no other chemical reagents—sulphuretted hydrogen, chlorine, hydrochloric acid (and other volatile acids) in the gaseous state or dissolved in water as chlorides of the alkalis or earthy metals—strongly favour its production. Thus, iron in an atmosphere containing oxygen, carbon dioxide, and water vapour is unattacked provided the vapour is not deposited in the liquid form upon the surface of the metal. Consequently in boilers and steam pipes, where these conditions are fulfilled by the steam being

super-heated and dry, no production of rust is possible. On the other hand, iron is unattacked at the ordinary temperature by water that is free from air, *i.e.*, oxygen and carbon dioxide, whereas at a high temperature—red heat—the iron becomes rapidly coated with an adherent crust of magnetic oxide, which acts as a protection against rust, and on this account the phenomenon has been utilised in the elaboration of a process for preventing iron from rusting. At moderate temperatures pure oxygen is inert towards iron, but under the influence of heat forms with it magnetic iron oxide. The same also applies to carbon dioxide, which has no action on iron in the cold, but at a red heat converts it into magnetic iron oxide and is itself simultaneously reduced to carbon monoxide. Even water containing oxygen alone, but no carbon dioxide, exerts no action on iron at the ordinary temperature, wherefore iron that is immersed in water containing air, but to which a little alkali or lime has been added in order to fix the carbon dioxide, will remain free from rust so long as any free alkali or alkaline earth is present in the water.

“As soon, however, as free carbon dioxide makes its appearance the iron is easily attacked at the ordinary temperature, and iron carbonate is produced, which is converted into the soluble form of bicarbonate by the excess of carbon dioxide. In this reaction hydrogen is liberated and will combine, to form water, with any free oxygen present. Given a sufficiency of oxygen and carbon dioxide, the whole of the iron will pass completely into solution, whilst in the event of a deficiency of these reagents the iron bicarbonate will be precipitated as iron carbonate, and carbon dioxide will be liberated. In presence of oxygen the carbonate is converted into the hydrated oxide, or true rust, and carbon dioxide escapes. The formation of bog iron ore—which has attained to such importance in the gas industry—is attributable to this process.

“The fact that in the formation of rust there is a continual evolution of carbon dioxide, which again exerts a destructive action on the iron, provided the other conditions—presence of air and moisture—obtain, explains to some extent the circumstance that, wherever a speck of rust is found, it continues to extend deeper whilst a nodule of rust appears on the surface. The principal reason for this development towards the interior of the mass is attributable to the circumstance that rust, like carbon and humous bodies, possesses the property of condensing gases, by superficial attraction, in which condition they may be regarded as nearly liquefied. Under these circumstances the gaseous elements, oxygen, hydrogen, and nitrogen, are endowed with considerable molecular mobility, directly encouraging chemical displacement and combination. The aforesaid property also accounts for the excellent purifying effect exerted on illuminating gas by bog iron ore, an effect which is not merely confined to the chemical process of modifying the sulphur compounds in the gas by means of the iron hydroxide in the ore, but extends also to the abstraction of carbon dioxide, carbon monoxide, and nitrogen from the gas.

“According to the preceding arguments the formation of rust is divisible into two stages:—

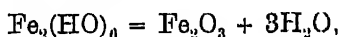
“1. Formation of soluble ferrous bicarbonate.

“2. Conversion of this product into white ferrous carbonate and progressively into iron hydroxide (hydrate), whilst, so long as oxygen is present, the liberated carbon dioxide continues to attack the iron.

“Of course the process is carried on in other ways whenever other chemical agencies come into operation. Thus when sodium chloride, calcium chloride, potassium chloride, ammonium chloride, or magnesium chloride is present, though even in but minute amount, a very considerable rusting naturally ensues, provided sufficient atmospheric

moisture is available. The process is greatly accelerated when the air contains sulphuretted hydrogen, ammonium sulphide, sulphur dioxide, hydrochloric acid, acetic acid, etc."

Schulte objects to the explanation of the formation of rust brought forward by Spennrath, by arguing, in the first place, that the rust formed on iron cannot be assumed to be accurately defined by the formula



although it is customary to do so, for the sake of simplicity. He considers that, since the formation of rust is a progressive operation, the mass to which that term is applied cannot exhibit a uniform composition, because the conjoint action of carbon dioxide in the process gives rise to compounds which afterwards gradually, and as a result of further changes, pass over into the form of the hydrated oxide.

Again, Simon explains that alkalis entirely absorb carbon dioxide only when the air containing it is passed through the reagent and agitated, so that only the stratum of air in contact with the liquid can be freed from its carbon dioxide by mere contact

"It is an actual fact that the co-operation of carbon dioxide can be traced wherever rust is formed, and Spennrath is greatly in error in denying this co-operation. However, the question whether carbon dioxide is or is not absolutely necessary is of no practical importance."

According to Mulder, iron under the influence of an acid, decomposes water at the ordinary temperature, the hydrogen being liberated, the oxygen together with that of the air combining with the metal. This applies also to carbon dioxide in solution; and, of late, ozone, traces of nitric acid and other substances have been included as active agents.

It may now be of interest to determine the conditions favouring the progressive development of an existing incrustation of iron rust.

On this point Spennrath states that "most metals when exposed to the air soon assume a coating, originating in a manner similar to iron rust; lead and zinc, for example, rapidly becoming tarnished. Every one knows, however, that lead and zinc can be left in contact with the air for any length of time without artificial protection. The aforesaid coating, when once formed, constitutes a fine skin which is perfectly impervious and completely protects the underlying metal from the atmosphere, and consequently from further attack. Should this skin be damaged or removed by scraping or other mechanical means, it is quickly replaced, the constituents of the air soon causing a fresh film to form on the surface of the metal.

"The behaviour of iron, or iron rust, is, however, quite different, the latter forming a porous mass instead of a coherent coating. This porous structure can readily be demonstrated by wetting a dry layer of rust with a drop of oil or petroleum, the liquid quickly penetrating into and extending through the mass. On this circumstance is based the well-known procedure of saturating rust with petroleum before scraping it off.

"All porous bodies, without exception, are endowed with the property of condensing, or occluding, gases in their capillaries. Iron rust being porous we may assume the presence of condensed oxygen in the rust pores. Moreover, rust has the power of absorbing and retaining water, and since this water will dissolve the condensed oxygen present in the pores, we may regard the liquid retained by iron rust as a concentrated aqueous solution of oxygen. This being the case the rust-forming power of the liquid will be increased, a rapid progression of the rusting necessarily following.

"From this point of view it is correct to say that rust produces more rust. It should, however, be borne in mind that the rust itself is not the actual chemical agency, it

merely acts as a carrier, losing its efficacy as soon as it is freed from water. It is therefore erroneous to reject iron oxide as a pigment for iron on the ground that it produces rust, since when it is suspended in oil, either in the liquid or resinified state, the oxide cannot condense oxygen nor can it absorb water.

"If iron rust, instead of being porous, formed a coherent non-porous coating, it would protect the iron just as well as the corresponding films do in the case of lead, zinc, etc. This is evident from the fact that so-called 'browned' iron does not rust, the coating produced by the browning treatment being nothing but rust, and only differing from the ordinary form in that it is compact

"Both the anhydrous and hydrated oxide of iron are generally regarded as carriers of oxygen. It is assumed that, in contact with organic bodies, they give up a portion of their oxygen, replacing this loss by re-absorption from the atmosphere. The proof brought forward in support of this opinion is, however, unconvincing. It is that when heated to redness with combustible substances, iron oxide readily yields its oxygen to them, in consequence of which this oxide may be employed for incinerating the more incombustible organic bodies. This behaviour, however, is not confined to iron alone, nor is it important. The combustion of organic matters in most cases results in the formation of free carbon, and on the other hand the generality of metallic oxides are reduced when heated along with carbon, *i.e.*, they part with some, if not the whole, of their oxygen. Many of them do this with greater readiness than iron oxide, the oxides of lead, copper, and zinc being easily converted into the corresponding metal by heating with carbon.

"If iron rust be boiled in a solution of grape sugar the former yields up a portion of its oxygen, a circumstance cited in favour of the action of rust as a carrier of oxygen.



"As a matter of fact, however, grape sugar abstract oxygen much more readily from other metals.

"Moreover, even if iron rust were actually able to attack organic bodies by ceding its oxygen to them, it would not be conclusive evidence that the same action is exercised toward metallic iron. Lead oxide, for instance, parts with its oxygen much more easily than iron oxide does; nevertheless we know that though a clean surface of metallic lead is rapidly coated over with a film of oxide, this layer does not increase in thickness, and consequently there is no transference of oxygen to the underlying metal."

Ebelin makes the following appropriate remarks on the subject under consideration:—

"It is true that a scientific explanation of the phenomenon has been proffered, but a subsidiary (or is it a main?) question has been left entirely out of consideration, namely, that some iron rusts readily, others only with difficulty, whilst some do not rust at all. For example, the unpainted iron chains on a fishing hut that came under observation were entirely free from rust notwithstanding their extensive exposure to both water and oxygen. Other iron articles become rusty without having been in the rain. How is this? If we examine an iron rod we find that it is mainly the parts uncovered by scale which rust. Is not this the point to which the lever should be applied? Should not attention be directed to preparing a kind of iron that will not rust, at least under paint?

"Furthermore we see in iron structures that, wherever iron chafes against iron, the rust regularly sprouts out. Perhaps this defect also could be obviated in the manufacture. It is a remarkable thing that a speck of rust will strike through a coat of paint like a smoke stain will through distemper on a ceiling. This is most plainly visible when a white paint is used. At first the stain is concealed by the paint, but as this

dries it is seen that the rust has rendered the paint yellow. Is the oil to blame, by dissolving the rust, or is it due to the small percentage of water present in every oil paint?"

There has been in the past a considerable amount of discussion and some differences in opinion as to the mechanism of rusting, in the first place as to whether rusting is due to chemical or to electrical action, and in the second place whether air or oxygen and water are the only essential factors, or whether carbonic acid in addition is necessary.

"W. R. Dunstan,<sup>1</sup> after a number of experiments, came to the conclusion that rusting does not take place in water vapour, in dry air, or in dry carbonic acid, but that rust is formed in contact with water if air quite free from carbonic acid is present. During the formation of rust, hydrogen peroxide is formed, which appears to be active in the further oxidation of the metal. The substances which will prevent rusting are those which destroy hydrogen peroxide. Carbonic acid, although not necessary to the formation of rust, is active in increasing the corrosion of the metal, the rust formed under its influence containing ferrous carbonate or bicarbonate. Electrical action is not regarded as necessary to the formation of rust although it may take place when the iron is impure or is alloyed with another metal; in this case the electro-positive portion of the metal becomes oxidised.

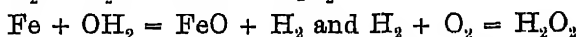
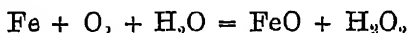
"G. T. Moody<sup>2</sup> is quite at variance with Dunstan, affirming that rust does not form except in presence of an acid. Carbonic acid is more active in this respect even than a mineral acid since during oxidation it is regenerated. The retarding influence of solutions of salts is not due to their activity in destroying hydrogen peroxide, but simply to the fact that carbonic acid is less soluble in them than it is in pure water, and hence is held in check more or less. Chromic

<sup>1</sup> *Proc Chem. Soc.*, 1908, 19 [267], 150-52.

<sup>2</sup> *Ibid.*, 1908, 19 [268], 157.

acid solution is especially useful in preventing rusting as it dissolves ferric oxide quite freely."

With regard to the formation of hydrogen peroxide during rusting, W. R. Dunstan, H. A. D. Jowett, and E. Goulding<sup>1</sup> view its formation as explained by one of the following equations:—



Dr. Edward Divers<sup>2</sup> in a discussion of the above results believes that the change is more nearly represented by the following:—

$(\text{O}_2 + 2\text{H}.\text{HO}) + 4\text{Fe} + \text{O}_2 = 2 (\text{HOFe}')_2\text{O}$  ferrous oxyhydroxide and  $2 (\text{HOFe}')_2\text{O} + \text{O}_2 = 4\text{HOFe}'''\text{O}$ .

"With reference to the action of carbonic acid he states that in six samples of iron rust, the proportion of iron present as ferric oxide varied from 51.12 to 68.89 per cent., as ferrous oxide 23.18 to 36.57 per cent. and as ferrous carbonate 7.93 to 12.31 per cent. of the total. His opinion is that rusting taking place under ordinary atmospheric conditions results in the formation of ferrous carbonate which progressively oxidises and becomes basic. A controversy then followed between J. N. Friend<sup>3</sup> and G. T. Moody and W. R. Dunstan<sup>4</sup> which need not be followed.

"Dr. W. A. Tilden, however, obtained the same results as Dunstan, finding that carbonic acid although it caused rusting was not entirely essential. He regards it as probably due initially to electrolytic action resulting in the formation of ferric hydroxide or carbonate. This he explains as due to the fact that iron consists of various components, which present surfaces at different potential when in contact with water, aqueous carbonic acid, or other electrolyte.

<sup>1</sup> *Journ. Chem. Soc.*, 1905, 87, 1548-74.

<sup>2</sup> *Ibid.*, 1905, 21, 251-53.

<sup>3</sup> *Nature*, 1906, 74, 540-54; *Journ. Chem. Soc.*, 1907, 23, 84.

<sup>4</sup> *Ibid.*, 1907, 23, 63-4.

"Rusting is inhibited by treating the metal with 1 per cent. solution of chromic acid or with strong caustic soda.

"C. F. Burgess<sup>1</sup> investigated the corrosion of iron from an electro-chemical standpoint and found that unequal strains set up electro-chemical action.

"G. T. Moody<sup>2</sup> replied to Tilden controverting his conclusions.

"J. A. N. Friend<sup>3</sup> figures an apparatus used in experiments which show that pure iron does not rust in contact with pure water and pure air.

"V. Andström<sup>4</sup> states that the action of carbonic acid appears to be only a secondary one, since the interaction of carbonic acid and metallic iron proceeds very slowly even in concentrated solution.

"W. R. Dunstan and J. R. Hill<sup>5</sup> advance arguments against the electrolytic theory that iron dissolves in pure water owing to electrolytic action. Instead of the theory advanced by Dunstan originally that hydrogen peroxide was an active agent in the formation of rust, it is now found that although it is formed to a slight extent it really is preservative in its action. It is stated that all materials which inhibit rusting render the metal passive, among these substances being chromic acid, potassium bichromate, chromate, bromide, iodate, hydroxide, carbonate, chlorate, ferrocyanide, and permanganate, hydrogen peroxide, barium hydroxide, sodium carbonate, borax, ammonia, but in very dilute solutions of alkalis rust forms readily.

"Lambert and Thompson<sup>6</sup> showed that pure iron does not rust in pure water containing dissolved oxygen."

Here the matter must be left, but it may be stated that

<sup>1</sup> *Trans. Amer. Electrochem. Soc.*, 1908, 13, 17-54.

<sup>2</sup> *Journ. Chem. Soc.*, 1909, 25, 84.

<sup>3</sup> *Ibid.*, 1910, 26, 179-80.

<sup>4</sup> *Z. Anorg. Chem.*, 1910, 69, 10-21.

<sup>5</sup> *Journ. Chem. Soc.*, 1911, 99, 1835-53

<sup>6</sup> *Ibid.*, 26, 290-91.

rusting which takes place under ordinary conditions is certainly due to some extent to carbonic acid.

The alterations to which iron is subjected in the earth were shown by a case where two lives were sacrificed through the breaking of a gas pipe, the rupture of which was effected by simple subsidence of the ground. The pipe was found to have been broken off clean, and exhibited, both externally

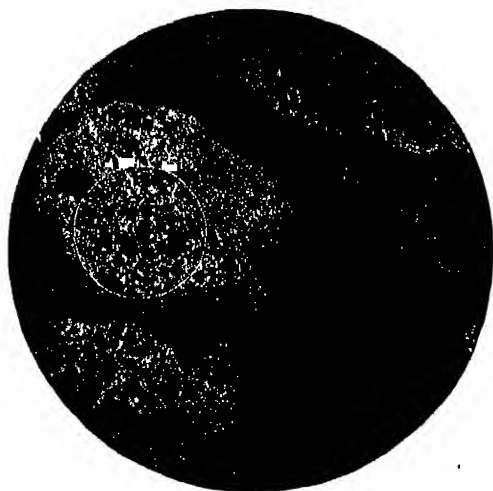


FIG. 1 (natural size).—Rust on rolled sheet iron, scoured with pumice, produced by falling drops of water constantly evaporated.

and internally, a thick incrustation of rust, the sound core of metal being not more than  $\frac{1}{16}$  to  $\frac{1}{8}$  inch in thickness

Another peculiar instance of the corrosion of iron was carefully investigated by Otto Herting. Here an old iron rail, a T-shaped girder, was found at Cape Breton in a mine which had been abandoned for about twenty years. The metal had a specific gravity of only 2.053, was greyish-brown in colour, could be cut and shaved with a knife, and powdered in a mortar, the powder being magnetic. Analysis furnished the following interesting result:—

Silicon . . . . .	14 20
Carbon (graphitic) . . . . .	24.10
Phosphorus . . . . .	5 85
Sulphur . . . . .	1.00
Manganese . . . . .	1.98
Iron . . . . .	81.50

It is thus evident that the film of iron silicate, known to be first formed when iron is allowed to lie in the ground, was incapable of preventing the destruction of the rail in question,



FIG 2 (magnified).—Rust on rolled sheet iron, scoured with pumice, produced by falling drops of water constantly evaporated.

and therefore cannot be regarded as an efficient protective coating for this metal.

As Professor L. von Tetmayr has adequately shown, the influence of smoke fumes on iron has not been sufficiently studied up to the present time, for we can see every day articles or objects that have, from the outset, been exposed to a strong acid corrosion without being protected from premature destruction by any smoke shield or the application of some suitable paint. Through a better appreciation of the state of affairs the system of construction employed in unfavour-

able cases in Bavaria of late is such that the ironwork is almost entirely enclosed in cement concrete, which alone should afford an extremely durable, acid-resisting coating. How great is the damage done to ironwork by sulphurous

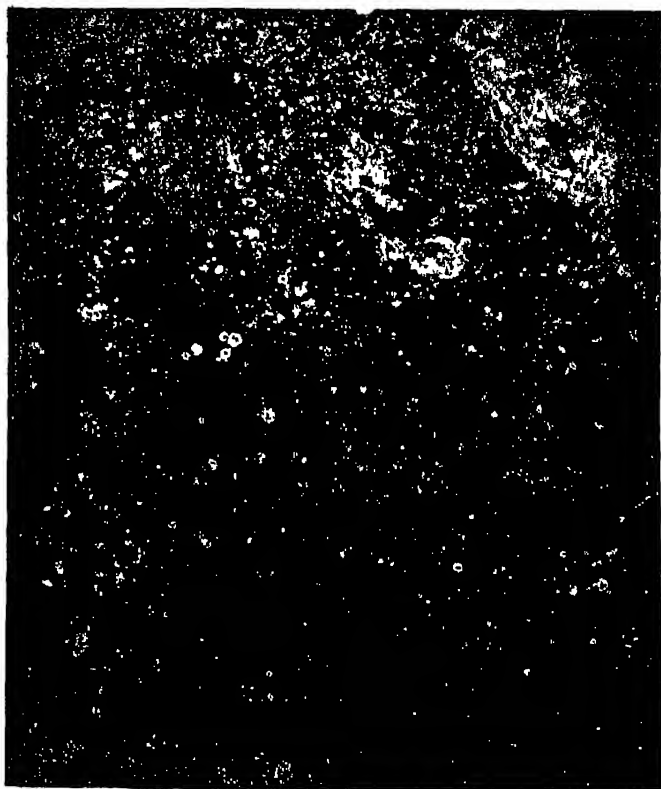


FIG. 3 (natural size).—Rust produced on rolled iron plate in twelve hours by moistening with water and leaving it to dry.

smoke gases is shown by numerous examples, a few of which are cited below :—

“In June, 1893, there was found in a corner of the abutment of the Swiss National Railway bridge where this line crosses the busy Aran track of the Swiss North-East Railway,

a steel chisel which had evidently been left there by one of the fitters sixteen years before. This tool was examined by me (von Tetmayr) and found to be completely rusted away. With the exception of the under side on which it had lain and which was rusted only to the depth of about  $\frac{1}{16}$  inch ( $1\frac{1}{2}$  mm.), the chisel was covered on all sides with a layer of  $\frac{1}{4}$  inch (6 mm.) and more of rust. Such an extensive corrosion of steel in the air could only have been brought about by the action of water impregnated with sulphurous or sulphuric acid, produced during the brisk traffic on the Aran line and deposited, with atmospheric moisture, on the acid-



FIG. 4 (natural size) —Iron plate with rust spots caused by water.

proof painted surfaces of the bridge, whence it dropped on to the tool in question."

Among the plentiful instances of the rusting of iron structures by the action of smoke fumes, reference may be made to that recorded in the *Revue Générale des Chemins de Fer*, June, 1893, p. 366.

Again, there are various street bridges on the Swiss railways which at present exhibit severe damage due to rust corrosion

District Engineer Ebert, of the Bavarian State Railways, reports the subjoined interesting case :—



“The bridge in the Central Station at Munich and the Cöppinger Strasse bridge at the Augsburg Station were both erected about the end of the sixties. The maintenance was of the usual kind, the ordinary oil paint being renewed from time to time. No special care was exercised in the selection of the paint or of the painters employed to lay it on, the injurious influence of the gases and vapour given off from the locomotives being then unknown. As in general, and especially in the seventies, very little consideration was bestowed



FIG. 5 (natural size).—Rust on rolled iron plate, produced in twelve hours by pouring water on to the plate and leaving it to dry. Rust flakes on clean metal.

on the question whether the use of iron for bridge building is not only cheap but also advisable, in view of the special conditions of maintenance exacted by the situation and method of construction, so there was little fear expressed that the smoke and steam given off by the engines would be likely to cause such an extent of damage as was actually found to exist, in the Cöppinger bridge in particular. Even in recent years when the question was raised at the invitation of the Bavarian State Railways, most of the railway managers

denied having encountered similar unfavourable experiences. Nowadays the opinion then expressed by the Bavarian State-Railway officials is universally held; this is particularly shown by the experience gained in America and published in the technical press. To resume the consideration of the question at issue, it must be observed that the maintenance and supervision of these two bridges was formerly, without doubt, carried on in a perfunctory manner. The traffic—especially that of shunting engines—passing under the



FIG. 6 (natural size).—Rust on rolled iron plate, produced by a single application of water left to dry on.

bridges precluded the employment of the ordinary painters' cradles, and the men were obliged to work on planks suspended from the longitudinal girders and, of necessity, extending but a short distance below the framework. Here their confined and cramped position, and the great personal inconvenience caused by the smoke and steam from the engines passing underneath, led them to get through the work with the utmost dispatch without much regard to thoroughness or the prescribed regulations. The removal of the soot and rust on the ironwork would certainly be very

inefficiently effected, and doubtless the paint was laid on damp places without previously drying them. Consequently a proper degree of hardening of the paint became almost an impossibility, since the steam from the locomotives was greatly retarded in its dissipation by the channels formed by the shape of the girders underneath, and would therefore be condensed on the surface of the iron. Such endangered portions were quickly coated over with a thick deposit of soot, so that in the course of the regular periodical inspection of the bridge the rust actually present was invisible to the



FIG. 7 (magnified).—Rust on rolled iron plate, produced by a single application of water left to dry on.

eye. When, however, in the year 1889, the thorough detailed examination of the Cöppinger bridge was undertaken, it was found to be so corroded in places as to necessitate immediate extensive repairs. On the removal of the top plates forming the roadway it became apparent that in many places, over the line, the cover plates, angle stays, and wall plates had become reduced in strength by as much as 50 per cent.; the angles of the vertical cross frames and the diagonal plates of the horizontal projection were in parts no thicker than a knife; and, in fact, some of these angles were mere stumps.

"In the Hacker bridge both the longitudinal street girders and the corrugated ( $\frac{1}{8}$  in.) iron plates were particularly corroded, the latter being quite eaten through in places. The damaged portions still exhibited, in section, the complete structure of the forged iron, and the smoked surfaces had a glossy black appearance. It therefore seems that not only rust formation, but also other and very extensive chemical changes had been produced by the constituents of engine smoke, sulphur dioxide, and so forth. No special investigation was, however, made.



FIG. 8 (natural size).—Rust produced on rolled iron plate by the action of concentrated hydrochloric acid for twenty-four hours.

"In order to protect the renovated bridges from these injurious ejecta, a cover plate of galvanised corrugated iron was placed under the Cöppinger bridge in 1890, and the whole of the longitudinal street girders and upper half of the cross girders of the Hacker bridge were encased in concrete, this treatment being applied to all the street bridges erected during the enlarging of the Munich Central Station. The aforesaid corrugated plates after being in position for three and a half years were found to be completely eaten through

in places over the sidings, but otherwise had fulfilled their purpose, *viz.*, the protection of the actual structure of the bridge. So far as the parts of the ironwork that were coated with concrete are concerned no unfavourable reports have as yet been received."

With regard to the action of lime, gypsum, and cement on ironwork set in fresh masonry, such as girders, ties, etc., the following particulars are supplied by experts:—

Ironwork embedded in fresh mortar soon becomes

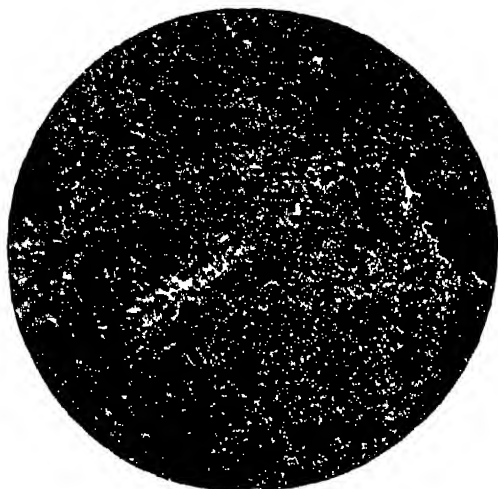


FIG. 9 (natural size).—Rust produced on rolled iron plate by the action of concentrated hydrochloric acid for twenty-four hours.

attacked to a considerable extent, especially the parts constructed of wrought or rolled iron, cast iron being less susceptible. The reaction shows itself first in the production of a strong coating of rust, which, moreover, is not confined to the surface but quickly extends towards the interior. Thus rust forms, in conjunction with the adjacent particles of mortar, regular scales, which are very brittle and chip off on bending or exposure to the slightest shock. In addition to this they absorb water from the surrounding mass of mortar,

thus contributing to the progressive destruction of the iron, a circumstance which explains why the oxidation proceeds with such rapidity that thin portions of the metal are entirely converted into rust within a comparatively short space of time. Moreover, the residual core of iron has undergone a notable alteration in its properties, the change being revealed in particular by reduced strength as well as by brittleness and shortness of fracture, its surface also often revealing a decided crystalline structure.

It is worthy of note that iron increases in volume concurrently with the progress of the rust formation, a circum-

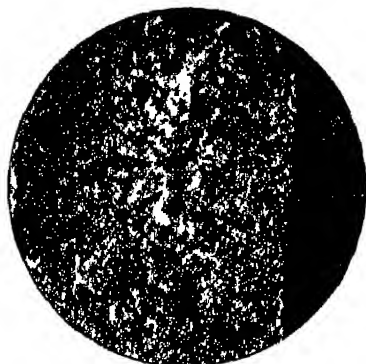


FIG. 10 (natural size).—Rust on rolled iron plate with defective surface, produced in five minutes by the action of dilute hydrochloric acid.

stance that may become a source of danger to the structure, on account of the very considerable pressure accompanying such expansion. Thus, for example, it has been observed that blocks of hewn stone fitted in a defective manner with iron dowels and clamps, and set in mortar, have become forced asunder owing to this expansion, the masonry then requiring resetting.

It is probably less generally known that gypsum exerts a similar though slighter effect on iron, manifested more particularly when the two materials are in contact in positions where they are directly exposed to the influence of moisture,

or in rooms filled with very damp air. The degree of force exerted during the expansion will be evident from the following

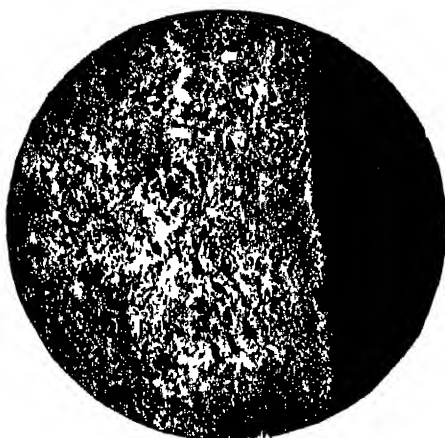


FIG. 11 (natural size).

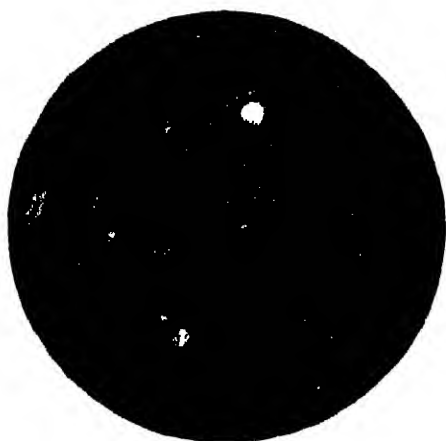


FIG. 12 (magnified)

Rust produced in five minutes on rolled iron plate, with damaged surface, by dilute hydrochloric acid, washed off with water and dried by heat.

instance: In hanging a wooden yard gate three hinge staples were driven into the red sandstone gate posts on either side,

two of them—the top and bottom staples—being set in lead whilst the middle one was plastered in, probably after the gate had been hung. After a time it was found that a conchoidal fragment of stone was chipping off on the inner side of one of the posts, without any apparent cause. This fracture left the plastered hinge staple exposed and showed the metal to be in an advanced stage of destruction, scales of rust  $\frac{1}{2}$  of an inch thick peeling off easily. The gypsum also exhibited a characteristic red-brown appearance. As, on in-



FIG. 13 (natural size).—Rust produced on iron plate by hydrochloric acid and ferric chloride.

spection, the door was found not to have exerted any pressure on this middle staple, the only remaining explanation possible of the splitting of the otherwise perfectly sound and veinless stone was the assumption that it was caused by the expansion of the metal in rusting.

On the other hand, pure cement has proved itself an excellent preventive of rust, iron set in pure cement remaining unruined even when kept under water. Painting iron-work over with a thin gruel of cement also answers very well,



and this coating, being at the same time cheaper, may be preferred to red lead (minium) paint.

The rusting of iron under atmospheric influences in general, and under normal conditions, has hitherto received as little thorough attention as that produced by the action of smoke fumes, weak acid gases, dilute liquid alkalis, etc. When iron is left in the open air, and thus exposed to the influence of depositions and condensations of water, rain, and snow, brought about by fluctuations of temperature, it rusts,



FIG. 14 (natural size).—Rolled iron plate with damaged surface scoured with pumice and rusted by the action of hydrochloric acid during two hours. The lower half was rubbed dry and consequently is less rusty.

*i.e.*, the iron—whether wrought or cast, rolled iron or steel—acquires a red incrustation, pulverulent when dry, easily rubbed off, and leaving a clean surface underneath provided the reaction has not occurred more than once and for only a short time. If, however, the deposition of water or moisture be repeated and prolonged, then the red layers increase in thickness, and when rubbed off leave behind them red and roughened patches, necessitating the employment of sharp instruments, forcibly applied, before the clean surface of the

metal can again be laid bare. By still longer exposure to the reaction, thick incrustations of rust are finally developed, and when these are removed the surface of the iron is found pitted with hollows of greater or smaller depth, the cleaning of the metal being then a matter of much greater difficulty. The author has examined a number of cast-iron gaspipes which had been left in the open for several months, and found that the formation of rust had proceeded far from uniformly, although the pipes were all exposed to precisely the same atmospheric conditions. Many of the pipes had



Fig. 15 (natural size).—Rust produced by dilute hydrochloric acid on iron plate with almost undamaged surface. The dark patch in the middle is where the rust has chipped off; and the dark line underneath shows where the layer of rust is peeling.

acquired only a slight film of rust, whilst others were almost free from rust on the upper side—the one most exposed to the rain—though the sides were covered with coherent, but thin, layers of incrustation. Even in one and the same pipe some portions were quite free from rust, whilst others, quite close, bore a fairly thick crust. It was in many instances easy to see where a raindrop had fallen, by the rusty patch, from which a long thin film of rust extended downwards along the surface of the pipe. The greatest development of rust was found usually at the ends of the pipes; projecting portions of the castings, as well as cracks and faulty places,

being also more extensively rusted than the plain surface. The degree of incrustation was relatively greater inside the pipes, indicating that the rust-forming capacity of moisture is greater than that of water in the liquid condition. The question why these cast-iron pipes gave such different results under identical conditions of atmospheric influence seems at first sight to be somewhat difficult to answer. It is most probable that the difference is attributable to the material itself. Most probably the susceptibility to rusting is dependent on variations in the composition of the metal at various points, blow holes, the rate of cooling, and con-



FIG. 16 (magnified).—Rust produced by dilute hydrochloric acid on an almost rust, undamaged surface of iron plate. The large patch shows where the rust has flaked off.

sequently the density, of the castings. That some or all of these factors have considerable influence is evident since the conditions under which the atmospheric influences acted were precisely the same in all cases, *i.e.*, the whole of the tubes, several hundreds in number, were exposed under absolutely identical circumstances and for exactly the same period of time.

The formation of rust under the action of atmospheric influences proceeds at a fairly rapid rate, though not so quickly as when the air is contaminated with smoke fumes, acid vapours, and the like. In such air rusting will take

place, even without the access of water—whether as condensed moisture or as rain—at a much quicker rate than in a purer atmosphere, its progress being still further accelerated by moisture, which dissolves these gases and condenses with them upon the metal

It is a well-known fact that ironwork in the vicinity of factories employing coal as fuel suffers considerably from rust, and that in the neighbourhood of chemical works, where



FIG. 17 (natural size).—Rust produced on rolled iron plate by the application of a solution of common salt left to dry on. The dark portion to the left was coated with linseed varnish.

gaseous acids are discharged into the air, all articles made of cast, wrought, or rolled iron are so rapidly attacked by rust, in fact in a very short time thin sheet iron is completely eaten away. This is easy to understand, for if even a weak acid be allowed to act continuously on thin sheet iron, the latter, in a comparatively short time, becomes brittle through the formation of rust, and finally corroded into holes.

The condensation of moisture on iron objects is also quite sufficient to produce rust and favour its progressive develop-

ment. The author examined an iron pipe which was kept through the winter in a perfectly dry place, and found that



FIG. 18 (magnified).—Rust produced on rolled iron plate by the application of a solution of common salt left to dry on.

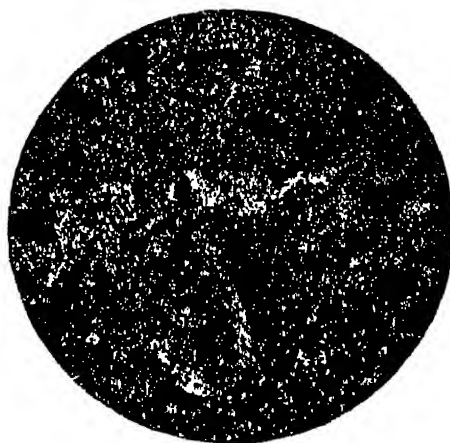


FIG. 19 (natural size).—Rust produced by common salt solution on rolled iron plate.

the moisture obtaining access to the room in the course of diurnal ventilation, floor cleaning, and respiration, sufficed

to develop on the surface, before the spring, a fairly uniform rough coating of rust. It is also well known that polished articles of steel or iron can be rusted by merely handling them once, the thin film thus produced increasing progressively as the articles are more frequently used, until finally an appreciable stratum of rust is formed.

The author has ascertained by a series of experiments that the action of water, acids, common salt in solution, and other rust formers does not produce a uniform effect on iron



FIG. 20 (natural size).—Rust produced on rolled iron plate by common salt solution.

plate. Under identical conditions and on different parts of the same piece of metal some places were found spotted with rust, whilst others were free therefrom, without any difference in the quality of the metal being discernible. Moreover, the rust flakes themselves were far from uniform in intensity and shape, so that, here also, much still remains to be elucidated, a thorough investigation of the governing conditions being necessary.

From the practical point of view the actual cause of rusting is a matter of indifference, it is likewise immaterial

whether carbon dioxide plays any part therein; we know that rust will form on iron, and we also know that 'rust, in whatever form it appears, is a dangerous foe to the metal.

It was once said by a practical man that "sooner or later every iron bridge must fall into the water," and even if this statement is not to be accepted literally, it nevertheless



FIG. 21 (natural size).—Rust developed on rolled iron plate by fourteen days' exposure to atmospheric action.

shows a full appreciation of the dangers incurred by iron structures, especially bridges subjected to heavy loads, if the formation of rust be not prevented by every possible means. On the occasion of the last great bridge accident (at Mönchenstein, near Basle), an expert stated that "it appears certain the bridge was not kept in proper condition, but

that rust, that foe to all iron structures, had been allowed to gain the upper hand. Under certain conditions the rusting away of a few rivet heads will suffice to dangerously weaken such a structure as this, possessing but a minimum margin of safety."

As a matter of fact it is not by the degree of rusting experienced by the massive components of iron bridges—such as the rolled girders, connecting pieces, stays, ties and such-like large and visible portions—that the safety and



FIG. 22 (magnified).—Rust produced on rolled iron plate by fourteen days' exposure to atmospheric influences.

strength of the entire structure is to be measured; but it is a question more particularly of properly preserving the smallest component parts, present in very large numbers. In all iron structures an important function is discharged by the rivets, which have to unite the individual plates, stays, girders, etc., which in turn are jointed, screwed, etc., together. If rust is allowed to gain a foothold on the rivets and screws the rigidity of the entire structure is imperilled. The rusting of one, two or more rivets in a girder, stay, etc., may not endanger safety, provided there are plenty of others still



sound ; but, if suitable care be not exercised, the whole of the rivets and screws may become rusted, a most dangerous thing to happen. If an invisible crack is sufficient, when filled with water and then frozen, to cause a large stone to split asunder, then a similar thing may occur with a rivet, a probably imperceptible space between the rivet head and the iron plate sufficing to admit water, set up rusting, and facilitate oxidation, so that in the course of years the rivet



FIG. 28 (natural size).—Rust produced on iron plate through ordinary wear and condensed moisture.

is entirely eaten away with rust, thus losing its hold and power of binding the parts together. If the same thing should happen with a large number of the rivets, then the stability of the structure is rendered uncertain and accidents of the worst kind may ensue.

Rust is an unwelcome visitor on all iron articles, but in

the case of iron structures, especially bridges, it is a dangerous foe, and one that should be combated by every available means. The manner in which this can be most effectually done will be thoroughly discussed in a later section dealing with the prevention of rust by painting, etc.

In preceding pages, a number of photographic reproductions of the appearance of rusted iron plate and other objects will have been noticed, and to these comes a further series requiring but a few words of elucidation. Under ordinary conditions, red-coloured objects, such as rust, appear dark coloured in a photograph; as the result, however, of experiments with various methods of illumination upon the iron plates here reproduced, it was found possible to obtain all the rust spots in more or less light-coloured tones, so that perfectly white spots indicate a strong formation of rust, darker tones showing less intense rusting, whilst the darkest portions represent the clean metal. Another important result, however, arose from these researches, that is, by means of the method of illumination and reproduction employed it became possible to reveal specks of rust undiscernible by the eye alone, or even when aided with a hand glass, a circumstance which may find still further practical utilisation.

When the forms in which rust makes its appearance are examined they will be recognised as varying in character. Thus, if a drop of water be placed on an iron plate (Fig. 1) the rust spot left behind on evaporation of the water corresponds in shape and dimensions to those of the drop. The colour is a rusty brown-red, with darker patches indicating that even in the case of a single drop of water the oxidation is by no means uniform. This is also evident from the variations in the thickness of the rust film, which, moreover, is interspersed with rust-free specks through which the clean surface of the unaltered metal is visible. On magnifying

(Fig. 2) these rust spots, although extremely thin, it will be noticed they already exhibit signs of flaking off.



FIG. 24 (natural size).—Rust developed on sheet iron in ordinary use as a stove pipe.



FIG. 25 (natural size).—Sheet of iron perforated by rust; the white patches are the holes, and the dark lines show the flakes of rust in the act of peeling off.

On leaving a stratum of water on the surface of an iron plate for twelve hours, and then removing the water by evaporation, a stronger development of rust is found which, especially towards the edges of the plate, is already comparable to a crust. In this case, peculiarly enough, the centre of the plate (Fig. 3) seems to be almost free from rust, only a few islets having formed. Peeling off is apparent on a more decided scale than in the previous experiment.



FIG. 26 (natural size) —Thoroughly corroded iron plate: atmospheric action.

By pouring water once over an iron plate so as to thoroughly cover the entire surface (Figs. 3 to 6) and then leaving it to dry, only a very slight film of rust is produced, the colour of which is uniform, though a number of spots are left clean and unruled. This test results in nothing remarkable since similar effects can be seen daily.

The application of concentrated hydrochloric acid, allowed to react during twenty-four hours (Fig. 8), causes the iron to dissolve as ferric chloride (Fig. 13) On lightly washing the

solution off with water and leaving the iron to dry in the air, a coating of rust, containing numerous contiguous rusty excrescences on a clean-etched surface of metal, is seen, these warty lumps being in places so closely packed as to simulate a crust. The colour varies from ordinary rust-red to dark brown.

The reaction of concentrated hydrochloric acid for twelve hours (Fig. 9) produces a coherent crust, of fairly regular



FIG. 27 (magnified).—Thoroughly corroded iron plate : atmospheric action.

depth, which has already shown signs of peeling off. Below this incrustation is a secondary formation of rust, so that when the upper crust falls off or is dissolved, a new layer will be found, which, however, takes much longer to arrive at the peeling-off stage.

When dilute hydrochloric acid is left to act for only a short time (Figs. 10 and 11) there is formed a coherent layer of rust of a fairly uniform dark rust-brown colour. Only in a few patches, where the surface produced by rolling has

been damaged, is the uncorroded metal to be seen. No loosening of the rust coating can be detected, a proof that it is relatively very thin.

In two hours dilute hydrochloric acid produces thicker incrustations of rust (Fig. 14) rather browner in colour. In this case also there is no indication of rust warts, neither has the peeling, shown in Fig. 15, yet commenced.

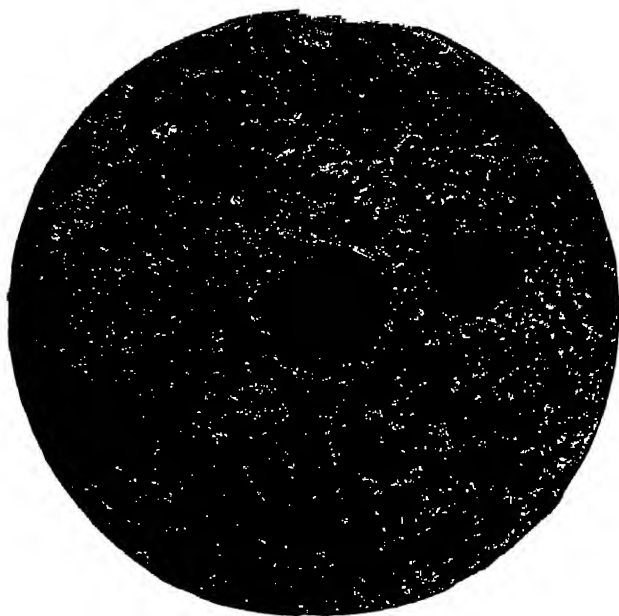


FIG. 28 (natural size).—Thick incrustation of rust developed on a wrought-iron disc by exposure in the open air.

The highly energetic action of common salt as a rust former is evident from Figs. 17 and 19, almost the entire surface of the iron in both cases being covered with a relatively thick crust, requiring but a very short time for its development. There occurs both a uniform surface of rust and individual rust warts; in this case also the peculiar phenomenon of a thicker incrustation round the edges is noticeable.

In all the preceding experiments, in which the artificial production of rust was effected in order to obtain an insight into the action of the different agencies, scarcely any further progression of the rusting has been observed, owing to the fact that the conditions of such development were lacking, the samples having been stored in a dry place. Only after the lapse of months could any alteration in the layers of rust be detected.

This extension makes itself evident in various ways. In all cases where the rust was caused by the action of water the increase was scarcely, if at all, appreciable after three months' storage in paper, this latter material being, as is well known, an excellent protection against rust. When rephotographed the plates exhibited no alteration and the rust had therefore made no further progress. In the case also of the rust produced by salt solution, the photographic picture taken after three months showed no alteration. Possibly the superficial crystalline layer of sodium chloride may have acted as a protective. The behaviour of the plates treated with hydrochloric acid was, however, different. Here the storage period of three months, even in a perfectly dry state, suffices not only for the complete separation of the upper layer of rust in the form of a coherent sheet as thin as paper, but also for the formation of a new thick underlying stratum



Fig. 29.—Wrought-iron pipe corroded in the soil.

which, although still adherent to the surface of the iron, will, in turn, peel off after the lapse of several months, the metal

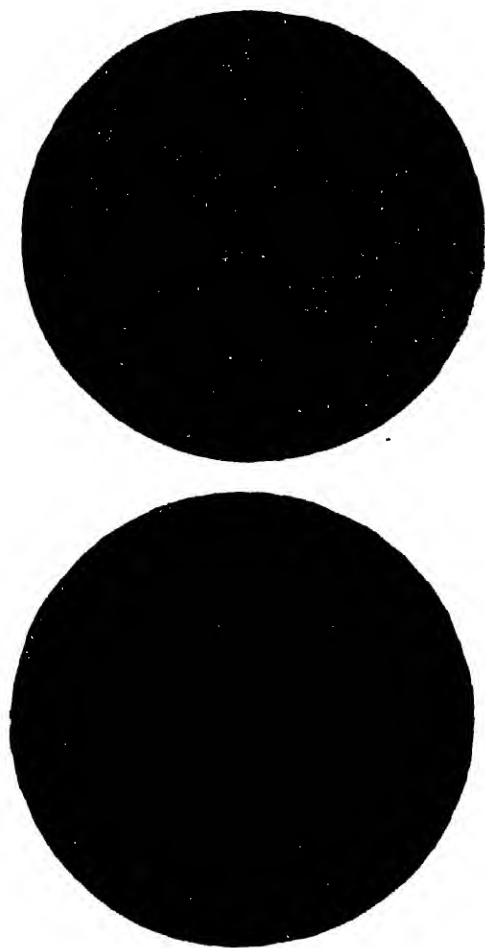


FIGS. 80 AND 81.—Rust pittings in tinned sheet iron stored for ten years in a cellar. The black patches are the rust, the lighter portions indicating the clean metal.

thus undergoing further corrosion. A decided progression of the rusting was also exhibited by the samples treated with dilute hydrochloric acid for a short period only; even the



application of a coat of linseed varnish—which was immediately absorbed by the layer of rust and thereby spread out in



FIGS. 82 and 83.—Rust pittings in tinned sheet iron after ten years' storage in a cellar.

the latter—proved incapable of preventing peeling, the crust in the portion treated being coherent and removable in a single piece.

With regard to the magnified views of these specimens it will be seen that in each of the reproductions marked "natural size" a white ring is drawn indicating the part magnified: hence the differences revealed by magnification can be readily seen by comparison with the original. In all instances the lightest patches indicate the palest-coloured portions of rust, the deeper tones the darker-coloured pieces, and only the black masses represent the still clean, unattacked metal

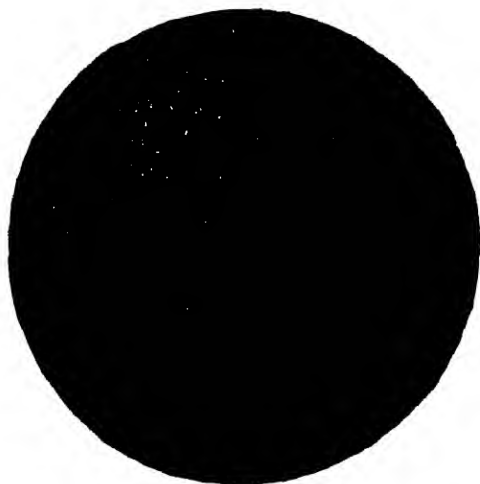


Fig. 34 (natural size).—Rolled sheet iron scoured with pumice and exposed for five minutes to the action of concentrated hydrochloric acid. The holes have been eaten away by rust.

Fig. 21 shows rust produced in the natural way, the iron plate having been exposed to atmospheric influences for fourteen days and nights in succession. Here again the phenomenon already referred to was observed, the metal being completely rusted over in some places, while in others only spots about the size of a needle point could be observed. In the first-named patches the formation exhibited the decided characteristics of rust in general, especially in view of the relative shortness of the exposure, the incrustation being even

more intense than that exhibited by the twenty-four hours' reaction of hydrochloric acid. A number of somewhat considerable rust warts of varying colour and thickness were formed. In this case in particular the photographs afford a decided proof of the damage that may be occasioned to iron by the action of atmospheric influences, and it is really incomprehensible that iron articles should be—as they frequently are—left lying exposed to the open air for weeks and months without any protection.

The progressive development of rusting naturally leads to much more serious consequences in comparatively thin sheet iron than in more massive castings. The former, when once actually attacked by rust, being entirely corroded in a comparatively short space of time, *i.e.*, the rust continues to extend and attack fresh, hitherto sound, portions of the metal, which finally becomes so far permeated thereby that it is rendered brittle, perforated with holes, and finally crumbles entirely away. An advanced stage of rusting is shown in Fig. 23. The rust forms thick layers—removable in the form of rust-brown powder when scraped with a knife—on the surface of the iron, which still retains some of its strength, though it will break if bent several times in the one place. Surfaces laid bare by scraping away the rust show either clean metal or rust pittings, the rust having changed colour, becoming yellowish-red, and flaking off in thick scales.

At a still more advanced stage of rusting, portions of the corroded plate easily break away—as shown in Figs. 24, 25—when touched, and holes are formed. Hence the cohesion of the mass—which, with the exception of a few unaffected patches, now consists entirely of rust—is destroyed. In the present case the rust is nearly black-brown in colour, interspersed with a few light patches, though a few individual fragments of iron appear to be still present in the mass, these

being, however, in a somewhat decomposed condition. The corrosion of sheet iron to such an extent as to form small, almost imperceptible holes, is almost invariably due to the action of acids; corrosion of this kind is often found on tinplate (Figs. 30, 31), the author having noticed it on tinplate bottles in which spirit or spirit varnish has been stored for some years, the tin coating being first loosened and the iron afterwards corroded in holes by rusting.

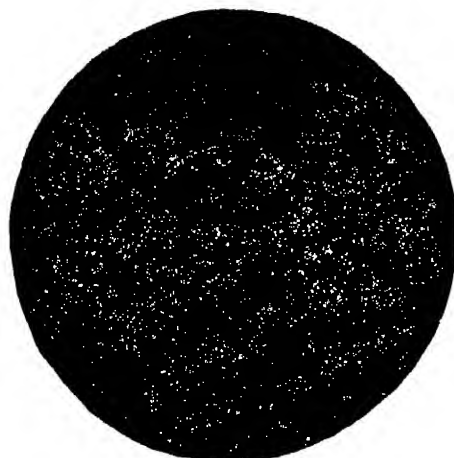


FIG. 35 (magnified).—Rolled sheet iron scoured with pumice and exposed for five minutes to the action of concentrated hydrochloric acid. The holes have been eaten away by rust.

A destructive action on sheet iron is exerted by the smoke fumes from coal fires, these causing the metal to fall prematurely into ruin. The causes having already been detailed, it is only necessary now to give a reproduction of a sample of such plate showing clearly the condition to which it attains.

An example of the complete corrosion of sheet iron is shown in Fig. 24, wherein a considerable number of rusty excrescences, resting on a stratum of rust already in the

peeling stage, are to be seen, portions of the underlying metal being also visible.

As will be evident from Fig. 28, no difference in form between the rust developing on cast and wrought iron respectively can be detected, rust warts and peeling off being met with in both cases; neither is any difference apparent in the incipient stage of rust formation.

Rust, as we have seen, makes its appearance as a thicker or thinner incrustation at individual points, and also in groups of rust flakes which, by increasing in thickness, become rust warts. The thickness of the layers varies according to the nature and duration of action of the rust-forming influences at work, often attaining to the dimensions of a millimetre ( $\frac{1}{8}$  inch) or more, and frequently manifesting a tendency to peel off as already mentioned. This peeling occurs in thin as well as in thick layers of rust, and, with the exception of extremely thin layers, appears to be independent of the thickness although more noticeable in the thicker layers.

The *colour* of rust is somewhat variable, being mostly a rather bright yellowish-red when newly formed, passing, with age and increasing thickness, into dark red-brown and even blackish-brown, though paler patches may still appear amid the dark layers. Very old rust is mostly blackish-brown and exhibits a more or less lustrous, almost crystalline appearance. When converted into powder the colour of rust is bright yellow-red, like that of the fresh product and the natural oxides of iron. Owing to the porous character of rust it readily absorbs water and considerably retards the evaporation of that liquid. It also easily takes up oily substances, which, on permeating the interior of the mass of rust, soften it and facilitate its removal by scraping. A similar effect is produced by petroleum, which property is taken advantage of in cleaning rusty iron by moistening it

## IRON-CORROSION AND ANTI-CORROSIVE PAINTS.

petroleum, then scrubbing with sharp sand, pumice, paper or emery paper.

Having now become acquainted with the circumstances under which rust is formed, and also having recognised the serious effect of rusting on iron, we turn to the question, how can rusting be prevented, and what means should be employed to this end?



96 (natural size).—Rolled sheet iron with apparently uninjured surface. No development of rust occurred after exposure to concentrated hydrochloric acid for five minutes.

In principle one might reply that the best remedy is to exclude all the agents which are capable of aiding in the formation of rust, *i.e.*, to keep out of contact with air (oxygen, carbon dioxide), water (in whatever form), acids, caustic alkalis, chlorides, and so on. To accomplish this, however, is impossible, since, in view of the multifarious uses to which iron and steel are adapted, it is manifestly impossible to exclude air and the other agents by any practicable means. There remains, therefore, no other course but to enclose or coat the iron with such substances which will keep the air

and moisture from actual contact with the metal, a matter of less difficulty than would perhaps appear at first sight, though the exclusion of acids, salts, etc., is more difficult, if not impossible, to accomplish. If we can surround the metal with some substance or material which while preventing the access of air and moisture, at the same time may be spread so thin that it leaves the form and outward appearance of the iron unaltered, then the problem is solved. Substances fulfilling these requirements do exist and have long been known; notwithstanding this, the permanent banishment of the foe has not been successfully accomplished, the reason for which is to be sought in the fact that these substances also in course of time are subjected to natural wear and tear, hence can only afford the requisite security for a certain period, their renewal being necessary when that limit is reached.

#### ADDENDUM TO CHAPTER I

In a paper read at a meeting of the Franklin Institute a few years ago, Mr. A. S. Cushman put forward his views as to the rusting of iron. It is assumed by him that iron first dissolves replacing the hydrogen in water, and that the oxygen then combines with the metal in solution to form rust, at the same time electrical charges which have been generated become neutralised. This action does not proceed uniformly over the whole surface of the iron but is localised to certain nodes or points. This is especially noticeable in the form of corrosion known as "pitting" in which local electrolysis has been most active, and where rusting to a considerable extent has taken place. That local electrolysis does take place can scarcely be doubted, otherwise the iron would go into solution evenly all over the surface. The conclusion is drawn that in order to prevent corrosion as much as possible the metal should be as free from impurities, and should be worked by heat and other treatment so as to render it as homogeneous as possible and to free it from any nodes at which positive or negative charges could be generated.

## CHAPTER II.

### RUST PREVENTING.

THE protecting or rust-preventing substances in general use may be divided, according to the purpose for which they are suited, into several classes, *viz.* :—

I. Such as afford a permanent preventive remedy against the formation of rust, irrespective of the expense and difficulty of the process of application. This object can be attained by :—

(a) Enamelling, *i.e.*, covering with a vitreous coating by the aid of great heat.

(b) Coating with other metals but little, if at all, liable to oxidation—zinc, tin, lead, copper.

The protection of iron and steel by deposition on its surface of a thin coating of metallic zinc, either by electroplating or by the process invented by Sherard Cowper Coles, is largely resorted to especially for small articles preliminary to painting. Iron and steel are also protected by nickel-plating and silvering.

Small quantities of other metals when alloyed with iron are known to profoundly modify its properties. This is also the case in relation to its liability to rust. Very small quantities of chromium, vanadium, tungsten, and molybdenum render the metal less liable to rust or to be attacked by acids, in fact a perfectly rustless steel is now being made by the use of chromium.

(c) Pickling or browning, *i.e.*, producing a layer of oxide or other compound on the metal, whereby further rusting is precluded for a long time.

II. Substances which will prevent the formation of rust for a lengthened period (the method of treatment being



limited by the dimensions of the pieces to be protected, and the expense and ease of application of the process). Enamel withstands the action of alkalis, chlorides, and even of acids, so that we have here at disposal a method capable of protecting iron from such agencies and permanently maintaining it in a rust-free condition. There are, however, two weighty circumstances which restrict the application of both enamelling and plating with other metals to a certain range of objects: first of all expense, and (in the case of enamel) the impossibility of treating articles above certain dimensions. The process of applying metallic coatings is expensive, while in enamelling difficulties are encountered due both to the large size of the parts used in some structures, *e.g.*, bridges, and to the cost.

Hence our interest is necessarily restricted to the categories II. and III., and these will be dealt with in the succeeding sections classified in the following order:—

1. Paints in general for use on iron.
2. Rust-preventing (anti-corrosive) paints; the conditions for their preparation and use.
3. Anti-fouling compositions (paints for ships' bottoms).
4. Other methods of rust prevention:—
  - (a) Rubbing over with fats, oils, or compositions based thereon.
  - (b) Various processes for obtaining protective coatings against rust.

To this class belong—

Coating with liquid or semi-fluid substances endowed with the property of drying hard, so as to form a solid integument preventing the access of air and moisture; painting with oil and other paints; coating with lacquers, varnishes, and tar or tarry bodies.

III. The protection of iron during transport or storage, up to the time it is to be put into use, whereupon the coating can be easily removed. This is effected by—

(a) Coating or rubbing over with solid and liquid fats or compositions which can be readily rubbed or washed off when the iron is to be used, and therefore exhibit but a very low coefficient of adherence to the metal.

(b) Graphite.

Spennrath divides the usual coatings applied to prevent rust on iron into such as are prepared by—

(a) Painting with oil paint

(b) Covering with solid or liquid fats.

(c) Painting over with tar or asphalt.

(d) Rubbing with graphite.

(e) Covering with other metals

(f) Pickling.

The classification previously mentioned is preferred by the author as affording a more correct representation of the various feasible processes for protecting iron from rusting.

The methods referred to under I. (a) and (b), *viz.*, enamelling and coating with other metals, will, experience teaches, give the most favourable and certain results, since they do actually completely exclude the metal from contact with air, oxygen, carbon dioxide, and water.

#### THE PROTECTION OF IRON FROM RUSTING BY THE APPLICATION OF VARNISHES, LACQUERS, AND OIL PAINTS, TAR, AND TARRY SUBSTANCES.

As expressed in the preceding section, we are taking as our starting-point the idea of protecting iron from rust as long as possible, consistent with the size of the objects, reasonable cost, and facility of performance of the process; this end being attained by coating the iron with liquid or semi-fluid substances endowed with the property of drying hard, so as to form a solid integument preventing the access of air and moisture.

When it is merely a question of simply protecting iron from rust, without regard to permanence, the object in view

can be attained in a very simple manner by painting the article over with a quick-drying solution of resin, a spirit varnish (lacquer), or a solution of celluloid. This method is easy of performance; the varnish dries quickly, and the iron, when not exposed to the weather, will be protected from rust for a reasonably long time. Lacquers of this kind are largely used for protecting iron and steel ware and utensils of various kinds, for which purpose they are eminently suited.

What we have in view, however, and now proceed to consider, is the protection of larger objects made of iron—iron structures such as bridges, iron buildings, etc. For this purpose a simple coating of lacquer which dries quickly but exhibits no sufficient powers of resistance is inadequate.

Since the application of iron to constructive purposes of all kinds, including shipbuilding, has attained such enormous proportions, attention has been directed to the provision of a sufficiently resistant covering for the metal. To some extent this has been found in oil paint, a mechanical mixture or pigment with linseed oil or linseed varnish, which, when laid in a thin coating on the surface of the iron, dries under the influence of oxygen, as a cohesive skin adhering to the metal. The continuity of the coating varies according to the pigment employed; and for a certain time the rust-forming influences are excluded from the metal, which for a longer or shorter period remains rust-free.

In the course of time, after a lapse of months or years, according to the pigment and the quality of the linseed oil or varnish, sundry changes in the constitution of the paint skin are induced by the influence of air and rain, its original elasticity is impaired, gradually giving place to brittleness, the mass finally attaining a condition in which, though still hard, it can be easily removed by scraping. Subsequently the residual mass becomes still further decomposed, the combination between the pigment and its vehicle, the varnish, being destroyed, and the former gradually removed by the

action of rain, wind, and the scouring effect of the dust raised by the latter, so that the iron is exposed and will naturally begin to rust under the usual influences.

The causes of this final destruction of the paint reside in the chemical alterations completed in the linseed oil or varnish, which have been attributed to the conversion of the elastic and cohesive linoxic acid into brittle linoxin. It is not the author's intention to enter more minutely into the question of the chemical changes occurring in linseed oil, varnish and paint; but, in view of the divided opinions prevailing on this point, he will confine himself to affirming the fact that all such coatings, whether composed of linseed oil, varnish or paint, inevitably perish, and that consequently no permanent protection, such as that afforded by enamelling, can possibly be attained. Moreover, no such permanence is expected in practice, a durability of two to five years as the maximum being held sufficient for a paint composed of good materials properly applied. Mention should not be omitted that it would be possible to prolong the life of a paint by drying at a higher temperature than usual (*i.e.*, 50° to 60° C.), this treatment rendering the coating unusually hard, resistant, and more durable than when left to dry in the air. The process is, however, beset with difficulties on account of expense and in convenience in application; moreover, it could not be employed in the case of iron structures already erected, since it is practically impossible to enclose an iron bridge, for example, in such a manner as to form around it a hot-air space for drying the applied paint. Consequently the idea not being feasible the painting must of necessity be carried on in the ordinary way.

Like many other substances both organic and inorganic, even the best oil paint finally undergoes decomposition; we are therefore restricted to the endeavour to elucidate the factors which will enable us to produce an anti-corrosive paint of the highest attainable durability.

The attempts made in this direction followed from the employment of iron for building purposes; it must, however, be stated that, on the one hand, requirements were exacted by consumers which it was impossible to fulfil, and, on the other hand, statements were made and claims put forward by some paint manufacturers, on behalf of their products, which to say the least were somewhat optimistic. Thus, for example, it is too much to claim for a paint that it will prevent the further extension of any existing rust on iron, or to expect a paint to permanently withstand the attacks of acid vapours or strong alkalis. Neither would anyone acquainted with the composition of oil paints expect them to be fireproof, seeing that he would be aware that every organic substance—and oil certainly belongs to this category—is combustible, and must therefore be destroyed on the attainment of a certain temperature. It is consequently unreasonable to exact of a paint requirements it cannot possibly fulfil.

It may be stated, however, with regard to the question of protecting iron from rusting, that the use of an oil paint, made from good materials, properly applied and renewed in good time, is still the best means available for the purpose of preserving iron structures. Moreover, the author is convinced this will long continue to be the case, for he cannot conceive any other coating endowed with the same qualities and yet easy to apply and renew. The question as regards iron is difficult, whereas it is easy in the case of wood, for the simple reason that two entirely different substances are under consideration, the one able to partially absorb the oil or varnish of the paint and thereby to render the subsequent coatings adherent; whilst the other, iron, being impenetrable, the paint is strictly a surface coating. Consequently paints for iron must be of highly adhesive character in order that they may not be liable to dislodgment, which if it occurred would defeat their aim. Another important factor is the condition of the iron previous to the application of the first coating.

The weight and dimensions of iron structures in general frequently precludes the possibility of keeping them under cover and sheltering them carefully from atmospheric influences; this undoubtedly affording the first opportunity for rusting to occur. This primary formation of rust rapidly spreads and increases in thickness; as we have seen that a single drop of water, allowed to fall on iron and then left to evaporate, is sufficient to produce a spot of rust, it is not surprising to find that rolled or cast iron is considerably rusted after a very short period of storage. This rust is, from the outset, the most powerful antagonistic influence to the resistant capacity of the succeeding paint, unless it is entirely removed before the latter is applied. Other contributory influences are also at work, among which may be mentioned the electrical tensions due to rust, referred to by Mulder in the following terms:—

“Like all other chemical reactions, rusting is accompanied by electrical tensions set up in the affected objects. An iron article may remain bright for a long time, but whenever any portion is attacked by rust the latter will very quickly spread over the entire surface. It is therefore essential, for the proper upkeep of the article, that all rust spots, however formed, should be, as early as possible, prevented from spreading; and to this end they ought to be painted over again at once, without waiting for all the old paint to disappear before laying on an entirely fresh coat over the whole surface.

“Then follows the method of protecting one metal by means of another, *viz.*, by bringing the metal to be protected into such a condition that it is less susceptible to attack. Thus strips of zinc or iron laid on the copper sheathing of a ship preserve the latter metal (Sir H. Davy's discovery), and steel knives and other articles can be also protected from rusting by strips of zinc.

“Such an application of zinc strips to large iron articles, whereby an intimate metallic contact is produced, cannot

prove otherwise than advantageous. A galvanic action is set up between the zinc and the iron, in consequence of which the former metal is more readily oxidised than the latter, and the iron is thereby protected from rust. A galvanic appliance of this kind must be laid on the bare iron, and the zinc must not be painted, though all the iron is coated over. A piece of zinc here and there will be sufficient, and they can be attached in inconspicuous positions, so that the appearance of article is not spoiled.

“This leads me to the consideration of the places of maximum corrosion in large iron structures, *viz.*, wherever two pieces of iron are attached together. If two strips of platinum be cut from the same plate, immersed in the same liquid, and connected to the opposite ends of the wire of a galvanometer, a current will at once pass. Exactly the same effect is produced between two pieces of cast iron from the same foundry, and even from the same furnace charge, and the action is the greater in proportion to the difference in composition between the two pieces of iron involved. Screws, nails, and rivets, form points of departure for the commencement and spread of rusting; it is therefore chiefly the points of attachment that must be protected in large iron structures. I am of opinion that, in general, far too little attention is bestowed on the accurate fitting of the connections, and that it is believed that an external covering, to be obtained by repeated coatings with paint, is sufficient. What I mean is this: that it is much better, for the attainment of durability, to cover the connections well and not paint the large pieces all over than to adopt the converse plan. Galvanic action always goes on between an iron screw-bolt and its iron nut; nevertheless atmospheric moisture is sure to find its way in between, even though the screw seems to fit quite tight. The first and principal care must therefore be bestowed on the fitting together of the sections. If on joining up two masses of iron end to end the latter are rusted,

the rust must first be cleared away ; the same applies to rivet holes, rivets, bolts, and nuts, such parts of the surfaces of all these as are to come together and cannot afterwards be reached by the brush from the outside being at the time of assembling coated carefully over with a protective medium capable of lasting as long as the surfaces are to remain in contact. The coating must also be thick enough to fill up all open intermediate spaces, a matter of no great difficulty in the case of bolts, nuts, and rivets, but one that requires specially suitable means in order to render the adjacent surfaces air- and water-tight where large pieces are in question."

Although this utterance of Mulder has brought us to a different stage of the question, we will revert to the point that all rust must be carefully removed from iron before painting. This object can be attained in several ways :—

1. By scrubbing or scouring with some hard substance, such as pumice, emery, sand, coke, etc.
2. Scrubbing with wire brushes.
3. Pickling with acid.

The first and second of these methods can be employed without the least risk of exposing the iron to further injury, the rust being removed by mechanical means, and nothing left behind to subsequently damage the paint in any way. The operation is often facilitated by the employment of substances able to penetrate the rust, which is thereby softened or loosened, and rendered more easy of removal.

To this class of substances belong the fats and oils, petroleum being especially preferred for this purpose. There is nothing objectionable in the practice, only that it is necessary to see that, after the rust has been removed, the surface of the iron is properly cleansed from any adherent fat, oil, or petroleum, since the merest film of oily matter will prevent the paint from adhering to the metal, and will moreover give rise to bubbles or retard drying. Oil or petroleum may therefore be used in order to facilitate the removal of rust.



from iron, provided the oil or petroleum is subsequently eliminated completely. Nothing is more inimical to the durability of paint on iron than an insecure adherence of the first coat to the metal.

The pickling operation with dilute acids (mostly hydrochloric acid) referred to under 3 affords a fair guarantee for the exclusion of rust, it is, however, attended with inconveniences of another kind. It may, for example, easily happen that the acid is not completely washed off, in which event the residual traces not only prevent the adhesion of the paint to the metal, but also give rise to the formation of rust underneath the paint and thus render the latter of no avail.

The instructions issued by railway companies with regard to the painting of ironwork frequently contained paragraphs to the effect that the pieces must be washed over with or placed in a bath of dilute hydrochloric acid, followed by a bath of milk of lime; they are then to be laid in hot water, and when removed will dry readily by reason of the temperature thus attained by the metal. Now experience teaches that such operations are not performed with the care indispensable to success, and it is therefore very easy—and probably of frequent occurrence—for the rust flakes to retain some of the acid liquor, which not only exerts an oxidising action upon the iron but also prevents the due adhesion of the paint. Pickling is a well-known operation, and there is no lack of opinions, favourable and adverse, on this subject. Here again reference may be made to Mulder's insufficiently known and still less properly appreciated work on *Drying Oils*.

Mulder also denounces the method of cleaning iron by immersion in an acid-bath, and says: "The layer of sub-oxide on the surface of both cast and hot-rolled iron plate should on no account be removed from large objects which

are exposed to wind and weather and are intended to be painted. On this account I must decry the method wherein iron castings are cleaned by immersion in a bath of dilute hydrochloric or sulphuric acid, and then treated with milk of lime and warm water to wash the acid away again. Cast iron is never entirely perfect, the surface always containing small channels and depressions wherein the acid water lodges, so that complete neutralisation by milk of lime cannot afterwards be attained. Consequently the acid will sooner or later make its presence known by the reaction set up. It brings the iron into a constant state of susceptibility to rust, and increases its electrical power. If one end of a piece of bright iron be dipped in dilute sulphuric acid the portion left exposed to the air will rust very quickly, whereas another piece of similar iron in an adjacent situation will remain bright. Since, therefore, it is the acids which so greatly tend to favour the production of rust, I hold that iron should be kept apart from them as far as possible." All iron that is intended to be painted must be absolutely dry, because no paint will adhere to a damp surface, especially when that surface is of iron. A distinction is here drawn between *damp* and *wet*, for it is absolutely impossible to apply a coat of paint to a wet surface of iron, *i.e.*, one covered with a layer—be it never so thin—of water, the paint simply refusing to adhere. On the other hand one *can* lay paint on a damp iron surface; only, when dry, the coat of paint does not adhere, and therefore has no stability, but flakes or peels off.

It is highly probable that this cause is at the bottom of many failures, since the labourers generally entrusted with the painting of ironwork can hardly be expected to understand the meaning of absolute dryness. Another factor influencing the moisture on iron is the difference in temperature between the metal and the surrounding air. In painting

ironwork out of doors, especially sheet-iron roofing, the condensed atmospheric moisture plays an important part. It may readily happen that with a cloudless sky the temperature of the iron may—by reason of its property of radiating heat—fall below that of the air. In consequence of this tendency, outdoor painting on iron in the early morning of a spring day is attended with particular difficulty, owing either to the metal being already coated with moisture or becoming so as the sun rises. The same thing occurs in the evening at sunset, at which time a fresh deposition of moisture occurs—especially when a rapid fall in temperature takes place—which covers the fresh paint with water, and tends to counteract the adhesion of the paint to the metal. Consequently, since work often must be commenced late and the coat must be dry early, it becomes necessary to employ very fluid and quick-drying paint, which must also be applied as thinly and uniformly as possible, otherwise rapid drying will not result. Painting should not be begun until there is no longer any risk of the condensation of moisture on the metal; and the paint must be so far dry before evening that it adheres to the iron and cannot be wiped off, *i.e.*, the formation of a deposit of moisture between the paint and the metal is precluded. Apart from the essential freedom from rust, care is therefore necessary to see that all rebates, rivet heads, grooves, and rivets are thoroughly painted, since it is in these that water is most apt to collect and cause the rusting of the already painted iron. To prevent the grooves, rivets, etc., themselves from rusting, they should be painted over before being put into position, in order to ensure that no portion of the metallic surface liable to be rusted by moisture remains exposed.

The conclusion to be drawn from these premises is that only perfectly dry iron, free from rust and all traces of adherent acid, should be painted, if it is desired that the first

coat shall possess that degree of adherence necessary to ensure the proper and durable union between the subsequent coats of paint and the metal. When the first coat does not adhere to the iron the following coats cannot do so, however well they may adhere to the primary one ; and consequently the entire layer will necessarily become loose.

The nature of the surface of iron varies, that of sheet iron, and the rolled plate principally employed for bridges and other iron structures, being smooth, though frequently exhibiting a pitted appearance through defects in the outer skin produced by rolling. Cast iron is more or less rough, according to the method of casting and the grain of the sand used in making the moulds ; and a rough surface presenting a large number of points of contact affords better opportunities for paint to adhere than a perfectly smooth one. The question then arises whether paint does really hold better to cast iron than to sheet or rolled iron ; and Mulder has also devoted attention to the query, Which kind of surface on iron is the best for painting—a polished and lustrous or a rough one ? According to this authority the question must be examined from different sides.

“ Since the paint cannot penetrate the metal, a rough surface ensures adhesion. By ‘ rough ’ I imply unevenness, not uncleanness. Such a rough surface consists of projections and depressions, the latter of which are filled by the paint, the points of contact, and consequently the adhesion, being increased just in the same manner as wood is held more firmly by a screw than by a nail. More than a clean rough surface cannot be desired for iron that is to be painted and then exposed to wind and weather, and upon which not only chemical but also mechanical influence will be at work. A coat of paint on rough iron will bend and contract when exposed to alternations of heat and cold, in just the same manner as paint on a smooth surface. The desired state of

roughness is mostly met with in cast iron, and this form of the metal I consider excellently adapted for painting on. However, thick plates and bars of rolled iron are now used for large structures, and these goods instead of being rough have smooth surfaces. They are nevertheless covered with a superficial blue layer which scales off on bending, and can easily be removed by scraping. This layer, which I term simply 'sub-oxide,' is produced during hot rolling and is really a mixture of iron with ferro-ferric oxide. It is useful in resisting the tendency to rust, but diminishes the adhesion of the paint. In the case of cast iron the sub-oxide is no longer pure but mixed with small particles of loam from the moulds, so that castings often exhibit a sandy appearance on the surface, and the question arises whether this also does not tend to decrease the adhesion of the paint. It is true that everything that can be removed from the surface of cast iron by scrubbing with wire brushes must be got rid of before painting; but whatever remains unloosened by this treatment has a greater degree of cohesion with the iron than any paint can possibly attain. The sub-oxide layer on rolled iron merits closer attention. Whether it should be removed or not before painting is a point on which opinions differ. I myself have eliminated this blue coating from the surface of iron by means of sulphuric acid, and found it a by no means easy task, requiring a good deal of labour and much acid. On washing the cleaned iron with a copious supply of water and drying it in the air, it will quickly acquire a thick coating of rust, whilst the untreated plates of the same iron remain perfectly free from rust. So far, therefore, the treatment with sulphuric acid is certainly disadvantageous, for the reasons already given. Finally the question of the advisability of removing the sub-oxide on rolled iron resolves itself into the following query: 'Does this protective layer become loosened after some time has elapsed?' If this be the case

it must certainly be considered injurious, though one is not therefore necessarily compelled to resort to acid. As a matter of fact it does break away in the thicker parts when the iron is bent, and also comes off after a while even when bending has not been practised. Since, however, all that loosens can be removed beforehand by scraping and scrubbing with wire brushes, I am of opinion that the use of acid should be discarded because of its undoubted highly injurious action."

#### BOTTOMING OR GROUNDING THE IRON.

Having now elucidated the conditions under which the preliminary preparation of iron for painting should and ought to be carried out, we will now bestow our attention to the grounding or application of the first coat of paint on the metal. We are here confronted by the question: "How, in view of the circumstance that the union of the paint and the substratum depends entirely on adhesion, is the operation to be performed?"

Originally and for a long period red lead (minium) alone was employed for this purpose, and even now the use of this pigment is frequently enjoined. The experience gained in the course of time with the substance in question has been very differently judged by different observers, and it is impossible to display the whole question clearly. The reason for this confusion is mainly due to the fact that the various observations on the durability of red lead grounding were not carried out with the necessary degree of accuracy, and that comparative experiments with this and other grounding paints are lacking. The following are some of the opinions that have been expressed with regard to the matter under consideration:—

Simon states that "red lead has been used for this purpose for many years, and has generally given satisfaction.

In gasworks, however, and wherever sulphur compounds, whether in the gaseous condition or in aqueous solution, occur, the employment of red lead, or of any other lead paint, is naturally precluded. Instances are also known where red lead paint has failed to answer, but they are somewhat rare, and the rusting or corrosion of the iron is, for the most part, attributable to other causes: defective preparation and cleansing of the surface, bad linseed varnish, etc. Opponents of red lead ascribe its alleged injurious action to electrical excitation, such as occurs in the union of lead with iron; but it is not proved that such a galvanic current can be induced when, instead of metallic lead, only the peroxide of this metal comes into contact with iron. If an abundant formation of rust did really occur under these circumstances, many thousands of instances of such destruction must have been recorded during the many years' practical experience that has been gained on this subject, and, in such event, the last word would certainly have long since been spoken on the matter."

The corrosion of iron observed by Jouvin is attributable not to red lead but to mercury oxide and mercury sulphate. These compounds were employed as an admixture to paint for ships' bottoms (anti-fouling composition) in order to prevent the development of the usual incrustations of *mollusca*, but their effect was to set up an electrochemical reaction, in consequence of which iron passed into solution and a crystalline deposit of lead was formed on the surface of the metal. The parts of the red lead paint that did not come into contact with sea-water remained perfectly intact.

With reference to the corrosion of iron by red lead, instances occurring on the keels of warships are mentioned by Jouvin in the following terms:—

"In the case of red lead paints, either simple or in admixture with mercury oxide or mercury sulphate, the surface

of warships, below the water line, becomes almost entirely covered with pustules of hydrated iron oxide. The pustules are shaped like a boil or tear, and occasionally blisters are formed resembling those developing in paint exposed to a hot sun.

"On pricking these blisters they are found to contain either air (?) or a liquid, the latter having a sour and astringent taste (iron chloride), and the bare surface of the iron is covered over with lustrous crystals of lead. Each blister has induced the formation of a lead tree, and is become a nest of crystallisation." Jouvin finds the liquid contained in the blisters to consist of a very acid chloride of iron, and he attributes the reduction of the lead oxide by iron to electrical action.

Simon originally formed the opinion that the mercury compounds present in many anti-corrosive paints set up an electrochemical reaction, but subsequently found the same development of blisters in paints containing pure red lead only. He placed a number of iron plates, coated with different kinds of paint, in an accumulator case, where they were immersed in a weak solution of ammonium chloride (sal ammoniac). The plates were also connected, by means of wires forming a closed circuit, with a few large Leclanché cells. At the end of a few days there developed on the plate painted with red lead a number of blisters, which, at first small, continued to increase in size, some of them hanging like tear-drops; in short, exhibiting precisely the same appearance as those observed by Jouvin on the keels of certain warships. The contents of these blisters also consisted of exceedingly acid iron (ferrous) chloride, and the surface of the iron was covered with beautiful lead crystals. This observation demonstrates that the corrosion of iron in this way is undoubtedly ascribable to electrical excitation. Hence the assumption that sundry



phenomena displayed in the case of paints on iron surfaces are due to electrical action would appear to be not altogether wide of the mark. The instance cited shows that on the one hand the pigment in the paint, and electricity on the other, effected the corrosion of the iron. It is nevertheless worthy of note that the red lead paint on the ships in question remained perfectly intact in the parts where it did not come into contact with water.

A. Landolt says:—

“Bottoming coats of paint of red lead or other covering pigment certainly exhibit the advantage of forming a good, quick-drying and hard layer, which adheres closely to the iron and also unites with the subsequent finishing coats. Their great covering power, however, is attended with a certain considerable risk, since defects and imperfections in the constructive material are only too easily concealed. Moreover, no information can be obtained as to whether the surface of the metal was really quite clean and free from rust before the first coat was laid on. The recommendation made by Professor von Tetmayr, that in future, in place of employing red lead or similar covering paints for bottoming, a perfectly transparent paint should be selected and used, is exceedingly appropriate and highly advisable. It should be possible—at least so experiments made on this point lead one to hope—to prepare a suitable painting material which will fulfil all the requirements of the case, *viz.*, quick drying, sufficiently tough and elastic, adhering well to the iron, able to absorb and unite with succeeding layers of paint, and exerting no injurious influence on the metal.”

Two principal defects are alleged against red lead as a bottoming paint: (1) That, in consequence of an insufficiency of oil or varnish, it rapidly dries up and becomes hard, the result being that the paint is quickly destroyed unless protected from rust-forming influences by a second superim-

posed coat of paint; (2) that it exerts an undue influence both on the underlying metal and on the subsequent layers of paint as well.

It is true that, of all the pigments hitherto known and used, red lead, owing to its weight, requires the smallest proportion of oil or varnish in order to form a distributable and efficient covering paint. A matter less generally known, however, even to those most interested, is that the protection afforded by the paint is entirely dependent on the properties of the linseed oil or varnish, and not at all upon the pigment which, however, must be incapable of acting on the same, *i.e.*, it must be inert and unalterable. This question will be more thoroughly discussed later; all that need be said at the present juncture is that the foregoing should be regarded as forming the fundamental principle in all paints for iron. Hence, no protective or rust-preventing properties—rust-destroying does not come into consideration, being an impossibility—can be ascribed to the pigments themselves.

We know that red lead forms a paint strongly adhering to and hardening on iron, which it preserves from rusting; we also know that the same paint is very durable when covered with subsequent coatings of good paint. On the other hand, red lead paint by itself, by reason of its small proportion of oil, soon perishes under atmospheric influences, and is therefore unsuitable for use as a finishing paint. There is another point of great importance in painting on iron, namely, it has been found by experience that although a paint rich in oil or varnish may be applied over a paint containing a high proportion of pigment to varnish, yet the converse practice is not to be followed; this is the reason why red lead is used as the primary and not the finishing coat. This experience primarily applied only to wood; it has been found also to hold good for iron.

For the most part the first coating with red lead is.

applied to the iron before it leaves the constructor's works, this being frequently stipulated for in contracts. It has, however, been found that under this first coat, rust may be present, though concealed and only making itself evident at a later stage, when so extensively developed as to show through the paint. Consequently in order to enable these rusty places to be detected immediately, it has been proposed to replace such covering paints by a coating of some transparent material which would allow the rust to show through clearly. Before proceeding, however, to the consideration of this proposal, we will deal with the manner in which bottoming iron with a first coat of red lead paint is generally performed.

In most cases, though not always, iron structures receive a first coat of iron oxide or red lead oil paint in the works when completed, *i.e.*, when the individual girders, stays, etc., have been riveted and brought into the most suitable condition for delivery. Attention, however, is rarely taken as to whether the girders have been riveted out of doors—where they are exposed to the air and, more especially, to the deposition of moisture brought about by fluctuations of temperature—or under cover; and still less is any thought bestowed on the painting of the rivet holes, the stems of the rivets or the underside of the rivet heads. In many works the paint is laid on by day labourers who simply daub it on often without suitable brushes, the work being regarded as properly done if the metal is outwardly covered over with paint. The author readily admits that painting the rivet holes, and the rivets themselves, is a very tedious and costly task, and that very often there is insufficient space available for the rivets to dry after painting. Nevertheless he holds that when it is a question of properly painting iron-work so as to fulfil the requirement that all parts of the metal shall be thoroughly covered, and that the connections, in

particular, shall be so carefully painted as to prevent the incursion of water, then all considerations of reducing the cost of production to a minimum must be relegated to the background.

It may readily happen in the case of iron structures that the saving of a few farthings per square yard in labour results in inferior workmanship, causing the object of the work to be defeated.

Turning now to the materials employed in the paint used in constructors' workshops, here again cheapness of the paint, or of the constituent pigment, oil or varnish, is regarded as the main desideratum, the seller who makes the cheapest offer obtaining the order, without any regard to the fact that considerable differences usually exist in the quality of the materials and that the quality depends upon the price obtained, not the price with the purity and suitability of the material.

For bottoming ironwork, either red lead or iron oxide (colcother) is prescribed, according to the opinion held by those in authority; which pigment is really the best for the purpose there are no reliable data available to show. Both vary considerably in quality, red lead being adulterated with heavy spar, brick dust, etc., whereby its value, covering power, and durability are impaired; whilst commercial iron oxide varies in its content of pure oxide from 70 to 98 per cent., its durability and value as a paint depending directly on the proportion of this constituent. Hence the causes of defects in the paints may to some extent be sought in the quality of the pigment employed. Greater influence, however, is exercised by the vehicle or medium—linseed varnish—and unfortunately we find too frequently varnishes adulterated with rosin oils and similar materials, which, on account of their cheapness, are displacing the pure oil varnish. Nevertheless, pure linseed oil varnish still remains unsur-

passed as a medium for pigments, not merely for use on iron, but for paints of all kinds. The pure varnish will last for a number of years, forming a solid elastic layer, impervious to wet ; whereas, if sophisticated with rosin oil or other substitutes, it becomes brittle and cracked within a short time after drying, allowing water to gain access to the underlying iron, and finally becoming pulverulent and easily rubbed off.

The first thing to consider, therefore, in the painting of iron structures is the composition of the paint materials ; and the operation should not be performed merely with the idea of covering the object over with a coat of paint which serves to conceal any defective places, but carried out in such a manner as to ensure the attainment of the object in view. Can the paint, however, be considered as in any way satisfactory when the man entrusted with the work merely stirs up the dry colour with some linseed varnish, in the paint-pot, by means of a brush, ignoring the proportions of the mixture which he then daubs on the iron as "paint" ? No one who knows that fine grinding is an essential condition for the preparation of a good paint can possibly regard such perfunctory treatment as satisfactory.

Consequently, the primary consideration in constructors' workshops ought to be to secure good materials for painting on iron ; and, secondly, that the painting should be done in such a manner as to really afford protection against rust, and not merely to comply with the letter of the customer's instructions, that "the iron shall receive a coat of paint". Naturally the operation will be rather more expensive, but the expense should be regarded as necessary in order that the tendency to rusting and its attendant danger to human life may be successfully combated. Some extremely interesting and noteworthy contributions on *The Preservation of the Iron of Iron Structures* have been made by Professor von

Tetmayr, though the author does not agree with all the views expressed therein.

"In my opinion," says von Tetmayr, "this matter has not been kept sufficiently abreast with the progressive technological development of the main subject, and reform seems to be necessary, especially since the introduction of forged iron for use in iron structures. A permanent supervision of the cleaning and working up of the iron is impracticable in the workshop, whilst, on the other hand, the employment of forged iron actually necessitates increased care in this respect. Bearing this in mind, contractors supplying such iron structures should be absolved from the necessity of painting the metal in the manner now customary, and instead be obliged to apply a coating of some transparent anti-corrosive composition previous to delivery. This ensures the advantage of the entire structure being accessible to inspection, whereby the quality of the workmanship can be more easily supervised, and rusty or otherwise defective places be cleaned and made good before the coating or covering of paint is put on. These advantages are lost when the iron has been bottomed with rust-coloured oxides, since these conceal accidental shortcomings, patches covered over with putty, and defects in the material, the colour of the pigment impeding the detection of rust, even when the outer coats of paint have been laid on thin and are of the appreciated light grey tint. Nothing should be used for bottoming but a light-coloured, quick-drying varnish of sufficiently elastic toughness, with good powers of adhesion and containing driers, the varnish being, moreover, free from added bases and from constituents capable of attacking iron. That iron structures properly varnished in this manner will withstand external influences, at least as well as those bottomed with the usual covering paints, is shown by the new bridge over the Neckar at Heilbronn, which was not painted until after the lapse of a year.

“If the structure has been well bottomed with a good drying oil, and the coating patched after mounting, the second coat can be applied. The paint employed for this purpose should be capable of being laid on thinly, endowed with good covering power and permanent adherent properties, sufficiently tough and able to resist atmospheric influences and the effects of variations of temperature to which it may be exposed on bridges crossing streets or railways, iron structures in busy cities and industrial centres, railway stations, etc., as well as to withstand the action of smoke fumes. The colour of this outer coat should be chosen with a view to facilitating the detection of rusty patches by contrast. If bottomed further in the usual manner, any good covering, readily distributable paint possessing the qualities of indifference towards iron, sufficient degree of toughness, durability and proper adhesive power, may be used, provided there is no question of exposure to smoke gases. On the other hand, if such gases come into action, the bottoming paint must, in addition, be endowed with a high capacity of resistance towards the influence of sulphur dioxide or sulphuric acid, and, moreover, be in all cases able to attract to itself, and permanently secure, the adhesion of the upper coat of paint. A sufficient degree of toughness or elasticity is necessary to enable the paint to follow, without injury to itself, the fluctuations in the length of the parts owing to the expansion and stress produced by heat and cold, wind and traffic, to ensure durability. When full consideration is bestowed on the difficulties in the way of thoroughly cleaning and properly repainting an iron structure already erected and containing a number of more or less inaccessible parts; when, in addition, the troublesome smoke, the influence of weather, and, finally, the moral force of the workman, are borne in mind, it will be convincingly evident that, other conditions being equal, preference ought certainly to

be given to the paints exhibiting the greatest durability through the conjoint effect of their resistance to atmospheric agencies, their adhesive power and toughness."

The injurious effects of atmospheric influences and alternations of temperature are already known; they are accentuated by careless workmanship or working in damp weather, and occasionally are induced through the defective adherence or by the brittleness of the dried paint—such paints cracking, curling up, and finally peeling off.

In concluding our remarks on this subject it is only necessary to add that there is a certain degree of justification in recommending the substitution of a transparent coating for covering paint on iron structures, previous to official inspection. In addition to red lead, iron oxide is used as a bottoming pigment for iron, and is unobjectionable. It requires a much larger proportion of oil or varnish than red lead in order to form a distributable paint, and therefore belongs to the richer class of paints.

#### BOTTOMING WITH LINSEED OIL OR LINSEED VARNISH.

Tetmayr's proposal to coat iron with a transparent layer of linseed oil or linseed varnish is not a novel one nor is it claimed as such. The method cannot be denied a certain amount of justification, if only for the reason that it allows rusty places to be readily detectable when delivery is taken of the ironwork. Many practical men, however, object to it on the ground that the coating does not dry hard, at least within a reasonable time; and because they fear that such a coating, covered by a layer of paint, would violate the canons of experience to the effect that a paint rich in varnish should never be topped by one in which pigment predominates, as it would lead to a rapid destruction of the paint by cracking and peeling.

Mulder, also, objects to the painting of iron with linseed



oil. He says: "Wood exhibits a great advantage over iron, since, on painting, it absorbs the paint, whereas iron is incapable of so doing. It is therefore advisable to apply a first coating of linseed oil to new wood, which is porous, the subsequent coat of paint coming into connection with the substratum; whereas iron, like all other metals, is devoid of this advantage, no penetration of the linseed oil or paint taking place, the mutual adhesion between the dried coating of paint and the metal being the sole means of connection between them. Hence it follows that the first problem to be solved in the painting of iron is, necessarily, not which paint sticks best on another coat of paint, but which paint adheres most firmly to iron.

"This question tends at the same time to cast doubts on the utility of boiled linseed oil as a first coating for iron. Linseed oil penetrates into wood and is therefore useful in this case, but as this does not happen in the case of iron, the utility of linseed oil is less for the latter material than for wood. Moreover, boiled linseed oil dries after a time but does not form a very hard varnish; the employment of this oil as a first coating for iron is therefore inimical to the adhesion of the after coats of paint. Hence it follows that iron should be coated with a paint which adheres firmly to the metal and at the same time dries hard, all intermediate layers being avoided. By using a fairly thin paint for the first application the results yielded by linseed oil can be more or less attained. The linseed oil of the thinner paint will penetrate into the pores of the iron [Mulder here is self-contradictory] just as well as pure linseed oil, because thin paint—whereby the ordinary consistency of paints for first coatings is implied—contains an excess of that oil.

"Since boiled linseed oil dries to form a not very hard layer of varnish, it cannot be anything else but prejudicial to the adhesion of the subsequent paint on iron; in such a

case the paint is separated from the metal solely by a layer of linseed varnish, and, especially since the latter is, according to instructions, applied to the warm iron, it fails to promote adhesion.

“This meaning will become clear if we imagine what would take place if the iron were coated with copal varnish. It is true that the residual varnish left by the drying of the linseed oil is tougher, and in this respect better, than copal varnish; still it is a varnish all the same. Now it is essential that the iron should be coated with a very adhesive paint, which will afterwards dry hard and fast, and that all intermediate layers should be avoided and dispensed with; consequently the use of linseed oil as a first coating for iron is to be discouraged. My own [Mulder's] view is that the use of this varnish for iron was selected on account of its suitability for woodwork, without the respective conditions of the two cases being taken into account, since, far from being applicable for metal, it is, as already stated, injurious.”

As previously remarked, no reliable results are available for reference, and no record of experiences in this matter has yet been made. Since, moreover, it is impossible to complete researches of this kind within a comparatively short time, the author has made a series of experiments with iron plates coated over with boiled, good-drying linseed varnish and afterwards painted with red lead paints, the drying of the plates under the usual conditions being replaced by drying at 60° to 70° C. Notwithstanding that many of the plates received several coats of red lead paint, which very quickly dried hard, none of the samples showed injurious results of any kind, and no cracks or fissures could be discerned with the aid of a magnifying glass; the author therefore believes himself justified in concluding that *the application of a covering of varnish to iron exerts no unfavourable influence on the*

*subsequent overlying coat of paint.* It must, however, not be forgotten that a thin covering of varnish is not the same as a coat of oil paint, and that therefore on this account no unfavourable action is likely to occur.

On the contrary, he holds that *to cover iron with linseed oil varnish is highly advantageous when the application is made in a very thin layer.* Such a layer will quickly set hard, whereas thicker strata remain tacky for a long time; the former is the more serviceable of the two, since the subsequent coat of paint will adhere just as firmly, with little or no risk of cracking.

In this matter of varnishing, the author would go beyond the proposals already made in other quarters, and recommend the production of an extremely thin layer of varnish on iron by laying it on hot, since in this condition the varnish exhibits greater fluidity and is well known to be an excellent means of preserving iron, drying much quicker and forming a much thinner covering than if applied cold. Moreover, greater care is required in laying-on cold varnish, on account of the increased tendency to form layers of irregular thickness; it may easily happen that the varnish on the vertical surfaces of a structure is dry long before that on the horizontal parts has ceased to be tacky, or still remains quite wet. It is well known that if linseed varnish be applied to a smooth horizontal surface as thinly as possible, and the article then turned on edge so as to bring that surface into the vertical position, a large part of the varnish will run off and be wasted. This reason alone is sufficient to render the use of a minimum quantity of varnish advisable; for the attainment of this object, it should be applied by rubbing the surface over with a rag dipped in the liquid. Even this slight coating will be sufficient to protect iron from rusting until such time as it is painted. It should also be applied to all bolts and rivets, as

well as to the larger parts of the structure, and it forms a very cheap method of protecting the smaller articles.

Thus, if a large number of bolts and rivets are placed in a sieve and then dipped into hot linseed varnish, left to drain, and afterwards dried in a room warmed to  $60^{\circ}$  to  $70^{\circ}$  C., the coating will be thoroughly dry in  $\frac{1}{2}$  to 1 hour, and, what is more important, it dries hard. Any further coat of paint will adhere well, thus precluding all danger of evil consequences arising during protracted drying.

In going beyond the recommendations made by others the author would also advise the employment of a temperature of  $50^{\circ}$  to  $60^{\circ}$  C. in drying the coating of hot varnish already proposed. He is of opinion that there can be no great difficulties in the way of arranging a hot-air chamber into which the varnished articles could be carried on trucks or rollers, and removed in the same manner on the expiration of the short time requisite for the drying process. By this means the objects aimed at in bottoming iron would be attained, *viz.*, the production of *an elastic and thin, but nevertheless hard and resistant, colourless coating, which facilitates the detection of any rusty patches present, and to which any subsequent coating of paint will firmly and securely adhere.*

#### FINISHING COATS OF PAINT ON IRON.

The principal part in the painting of iron is the application of the first coat, since, unlike wood, there is no absorption of paint into the pores of the substructure, the adhesion of the subsequent coats is necessarily restricted to the surface of the paint or varnish already in position; consequently everything depends on the latter.

When iron-, or lead-oxide paint, or linseed varnish alone is employed, an opportunity is afforded of making good any defects, in the application of the second coat of paint. These

defects are most likely to occur on the parts most difficult of access, and where consequently the carelessness of the workmen has a wider scope. Among such places may be mentioned, for example, the under and inner sides of girders, bolt heads and nuts, rivets, etc., just precisely where extreme care in painting is necessary to prevent the subsequent incursion of water. A proper check over the workmanship can be secured by choosing paints of different gradations of tone for the several coatings, a step which will enable defective places to be detected.

All coats of paint require a certain time to dry, the exact period ranging from six to thirty-six and even forty-eight hours. This does not, however, mean that the paint is hard by that time, although it is dry, *i.e.*, no longer tacky when touched, it may still yield to the pressure of the finger, and if the hand be placed on the painted surface for some time an impress will be left behind on withdrawal, owing to the softening of the paint by the warmth and pressure. After a longer or shorter period of time has elapsed, however, this condition disappears, the paint having become hard. The hardening is effected partly through the absorption of atmospheric oxygen, by which the drying oil is converted into a hard, brittle substance, and partly also in some cases on account of the action of the pigment on this dried layer of linseed oil or varnish. Pigments of this kind include all the lead colours, red lead, white lead, etc., which combine with the oil varnish quickly forming a hard mass, the degree of hardness being the greater on account of the preponderance of pigment over oil in the paint.

On the other hand, some pigments, such as iron oxide, graphite, zinc white, and many others, require much larger proportions of oil or varnish in order to form a distributable paint, and these pigments have no influence on the harden-

ing of the paint, since they do not enter into combination with the vehicle or medium. The presence of this larger percentage of linseed oil, or linseed varnish, in such paints renders them much more suitable as finishing coats, since the medium is retained in a soft elastic condition for a longer time, and is better able to conform, without injury, to the expansion and contraction set up in iron structures by changes of temperature.

The following opinions of experts on the suitability of different pigments for painting on iron may be cited.

With regard to *white lead*, Dr. A. Landolt says :—

“ White lead, used alone and in a pure state, is not a good paint for ironwork. Apart from the fact that the pure white of the pigment will speedily become impaired and dirty, the paint also sets very hard in a short time, the elasticity disappears, and cracks are formed. For this reason white lead is mixed with other substances, in the first place to impart colour to the paint, and furthermore for the purpose of increasing its power of absorbing oil, this latter, or linseed varnish, being the principal agent determining the durability of the coating.

“ The more oil required by a pigment in order to produce a distributable paint, the better will it be adapted for use on iron, especially in the open air, provided it satisfies the other conditions, of covering power, neutrality, and capacity of resistance to acids.

“ For the same reasons,” says Landolt, “ that operate in the case of white lead, red lead paint is unsuitable as a finishing coat, particularly where the final or tone coating has to be laid on at once or after a relatively short time.

“ Red lead paint soon becomes very hard, and cracks under the influence of the air. An old and well-proved rule teaches that bottoming paints in all cases, and especially on

iron, must be hard and low in varnish, in order that the following coat of paint, richer in varnish, may be durable. Red lead forms a paint poor in oil, quickly setting hard, and endowed with great adhesive power, on which the subsequent coat of paint will adhere strongly."

Mulder (the author of the work on drying oils already referred to) expresses himself on the use of *iron oxide* as follows:—

"Iron oxide, when mixed with oil, is a perfectly neutral body, without the least influence on the drying of the oil, whether the latter be raw or boiled, even when the mixture of oil and oxide is heated to 100° C. for two consecutive hours. Consequently, in this respect iron oxide is of very little value as a pigment. [This is incorrect; it is only as a drier that the oxide is of no use.] The same also applies to zinc white. On the other hand, white lead and red lead greatly assist the oxidation of linseed oil, the last named in particular acting both by the lead oxide it contains and by an actual surrender of oxygen.

"Practice confirms this [and also that Mulder started with the erroneous assumption that the pigment, to be good, must necessarily exert a drying action]. When boiled oil, whether alone or mixed up as paint along with some neutral substance like iron oxide, zinc oxide, etc., is left or kept in an open vessel, a skin forms on the surface. With white lead or litharge this skin forms sooner and attains a greater thickness; red lead paint sets to a thick mass in the vessel; and, whilst putty made solely from chalk does not become hard even after several months, it very soon hardens if white lead be present, and white lead putty quickly sets as hard as stone, even when kept under water."

With regard to iron oxide Landolt states that this substance "uniting with a much larger proportion of linseed

varnish should, when used as a bottoming paint, receive an addition of oil of turpentine; *i.e.*, the first coat should be low in varnish, the final coat richer. The poor results obtained

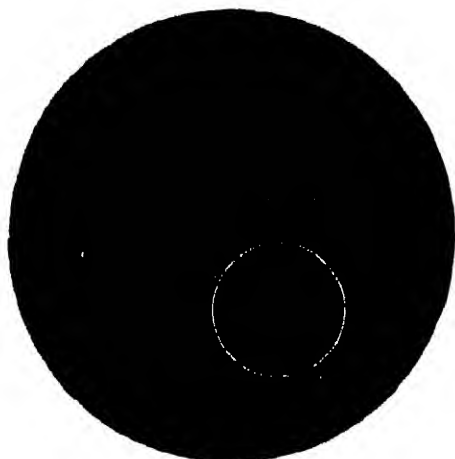


FIG. 87 (natural size).

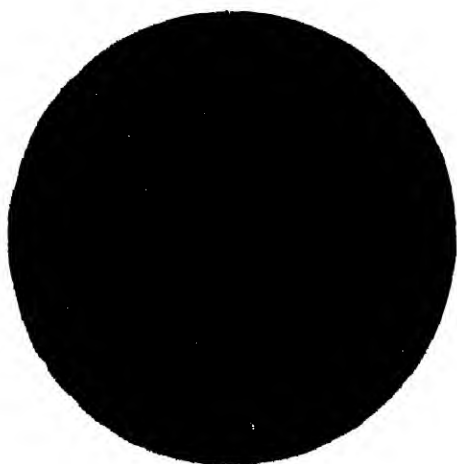


FIG. 88 (magnified).—Fine (hair) cracks in a ten-year-old white lead paint.

with iron oxide paints may, when bad materials are used, be very often due to the non-observance of this rule."

Further references to the utility of a large proportion of



oil or varnish in paint will be made in the following section on "anti-corrosive paints".

Every oil paint, no matter whether the contained pigment absorbs much or little oil or varnish, in time comes to destruction. The actual period, however, at which this occurs varies, depending on the amount and quality of the varnish used. All paints perish at some time or other, either as a result of cracking, or in consequence of progressive oxidation,



FIG. 89 (natural size).—Blisters, formed by warmth, in a red lead paint poor in varnish, topping a richer bottom coat. The blisters have burst, collapsed, and left the metal bare.

leaving the paint finally in the condition of a powder loosely adherent to the substructure. The cracks are at least quite as prejudicial to the preservation of the iron as the coherent but permeable coat of paint, since they admit moisture to the metal and engender rust, whilst the more or less absorbent paint also takes up and retains water, and may therefore also give rise to its formation. Hence, in order to ensure the preservation of the iron, the formation of cracks must, as far as possible, be obviated by the selection of paint

of a suitable character. When, however, cracks have once commenced to form, a fresh coat of paint must be laid on at once, and this also applies to cases where the paint has perished, a condition easily recognised by the dull earthy appearance of the coat and the ease with which it can be removed. In this respect no difference exists between the two, except that a layer of weathered paint is capable of taking up a good deal of oil or varnish, and the formation of

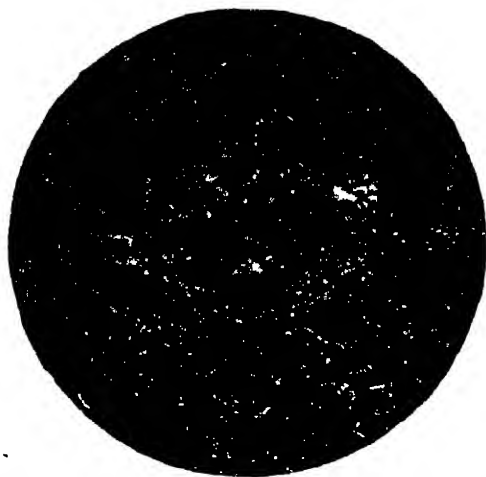


FIG 40 (magnified).—Blisters, formed by warmth, in a red lead paint poor in varnish, covering a bottom coat rich in oil.

cracks is entirely precluded, whereas in the other case this is always liable to recur.

The time taken by oil paints in drying has already been stated as from six to thirty-six, and even forty-eight hours, depending on the drying properties of the oil or varnish, the influence exerted by the pigment, and, last, but by no means least, the external conditions of temperature and weather. It may also readily happen that the same paint may dry at one time in six hours, but require at another time twelve hours and even longer. This variation is brought about by

the warmth and moisture content of the external air, paint that normally dries in twelve hours drying in six hours under a hot sun and in a good draught, whilst in foggy weather it will still be wet at the end of twenty-four hours. This fact, and also the drying influence of the pigments, has been demonstrated by innumerable experiments. Thus white lead and red lead, ground up with linseed varnish which by itself dries in six hours, cause it to dry quicker, *e.g.*, in five hours;

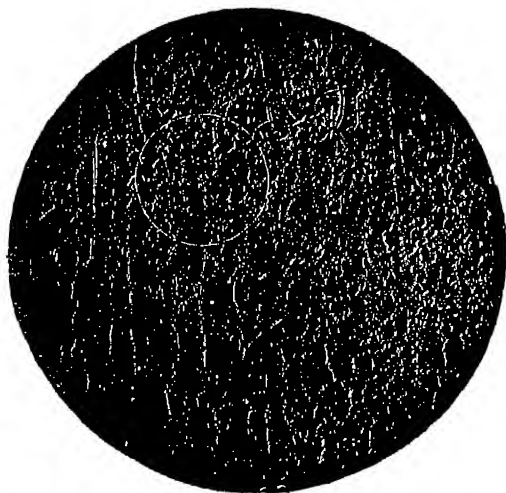


FIG. 41 (natural size).—Cracks in an oil paint, with another, intermediate layer.

whilst on the other hand the incorporation of ochre or iron oxide in the same varnish will produce a paint taking twenty-four hours to dry; there are also other pigments, lampblack for example, which will prevent this otherwise fairly quick varnish from drying at all when used as paint. The pigment, as well as the conditions of temperature and moisture, must therefore be taken into account in testing the drying capacity of a paint.

With regard to the behaviour of a pigment, its capacity for absorbing linseed oil or linseed varnish, and its influence

on the drying and hardening of the paint, the most suitable paint for the preservation of iron structures will be the one that contains a pigment requiring a large admixture of linseed oil or linseed varnish in order to render it distributable, and which exerts no influence, favourable or the reverse, on the drying and hardening of same.

In applying paint to either wood or iron the following rule holds good :—



FIG. 42 (magnified).—Cracks in an oil paint, with another, intermediate layer.

*Each previous coat of paint must be perfectly dry before the following coat is laid on.* If a fresh coat be applied on one that is not yet quite dry, risk is incurred of the paint being drawn, under the influence of heat (the sun), whereby blisters are produced. These may vary in depth, and should they extend to the first coating may leave the surface of the metal exposed, so that when the paint cracks, under mechanical influences or on further drying, the unrestricted admission of moisture to the iron ensues. Hence rust inevitably follows, which, as it progressively increases, lifts the

paint from the iron in many places, and finally causes it to fall off. The manner in which this blistering in paint is affected, by the action of underlying rust, can be seen from Fig. 17, where a simple coat of varnish was laid on a rusted sheet-iron surface. The varnish sank into the comparatively thin layer of rust, which it lifted up so that the surface became covered with a large number of small bubbles, which could be loosened by touching them and then left the



FIG. 48 (natural size).—Effect of water on wet paint, with immediate formation of rust.

rusty surface of the metal exposed. It is asserted by some that the practice of bottoming iron with linseed oil or linseed varnish, contributes to the formation of blisters, but this the author would deny, since he has been unable to detect any such blistering; and he believes rather that it only occurs when the sun has acted directly and continuously upon the paint for a fairly long time.

The presence of intermediate layers of other paints is highly inimical to oil paint on iron. It seems very improb-

able that any one would apply a coating of size paint over oil paint; nevertheless, such a thing is *possible*, and, owing to the modern tendency to effect economies by the use of cheap materials, it might possibly occur.

Figs. 41 and 42 illustrate the condition induced in a coat of oil paint when a bottom coat of red lead paint has been covered with a layer of size paint, and this again topped by a coat of red lead paint. It may be stated in this connection



FIG. 44 (magnified).—Effect of water on wet paint, with immediate formation of rust.

that from considerations of economy wood is frequently painted over with a coating of size paint before the oil colour is laid on.

Just as in the case of a first coat on iron, the subsequent layers of paint *must be laid on only when the surface is perfectly free from water and moisture, and must be equally protected from water and rain.* The effect of a layer of water upon a perfectly fresh coat of paint can be seen in Figs. 43 and 44. Here the fresh surface of the paint was suffused

with water, whereupon a portion of the paint collected on the surface of the water and ran off, whilst the rest remained on the iron, but no longer as a coherent stratum, part of the iron surface being laid bare. Partial contraction of the paint also set in

The action of fine rain-drops is illustrated in Figs. 45 and 46. The paint was not quite wet, but still far from com-

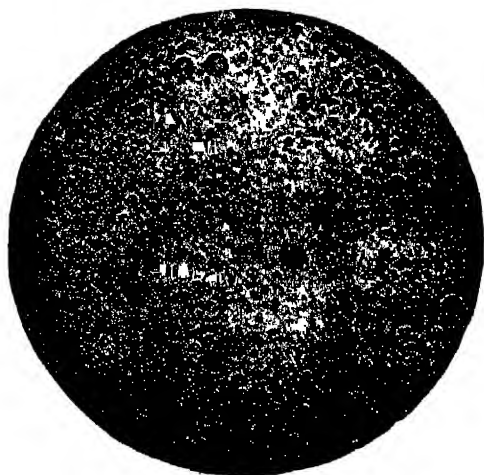


FIG. 45 (natural size).—Effect of fine spray on a wet layer of oil paint.

pletely dry, when the drops impinged upon it; and their impact partly dispersed the oil colour, thus giving rise to a whole series of depressions, which in the case of horizontal surfaces would afford a more or less permanent lodgment for the water, and facilitate its penetration into the layer of paint.

#### APPLYING PAINT.

In the case of iron, as in painting on other surfaces, it is also necessary to *lay the paint on as thinly as possible consistent with covering the object, and on no account should the coating be so thick as to form a wrinkled instead of a smooth surface on drying.* If the paint be laid on too thickly it will

spread evenly, in accordance with its natural tendency, but does not dry in a normal manner. The upper layer skins over before the underneath parts have begun to dry, and when drying ensues throughout, the skin contracts forming wrinkles and folds, which spoil the smoothness of the surface and at the same time present an opportunity for the retention of rain water and condensed moisture. In the end these wrinkles and folds easily split, thus enabling the water to

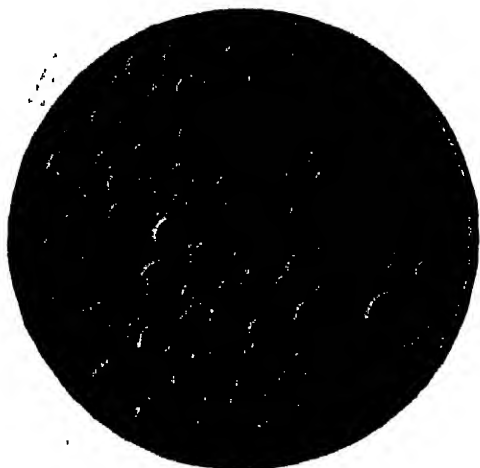


FIG. 46 (magnified).—Effect of fine spray (rain) on a wet coat of paint.

gain admission to the inferior strata of the paint, whereby the durability of the coating is imperilled.

The number of coats of paint required to protect the substratum depends on the covering power of the paint. This power implies the quantity of paint necessary, per given unit of surface, to completely mask the colour and superficial characteristics (not form) of the underlying material.

Now the various pigments differ considerably in covering power; but the matter must be regarded from two stand-points, it being preferable to speak of *absolute* and *relative* covering power. To take one example, white lead possesses



a greater *absolute* covering power than zinc white, but the *relative* covering power of the latter exceeds that of the former; that is to say, where weight is left out of the

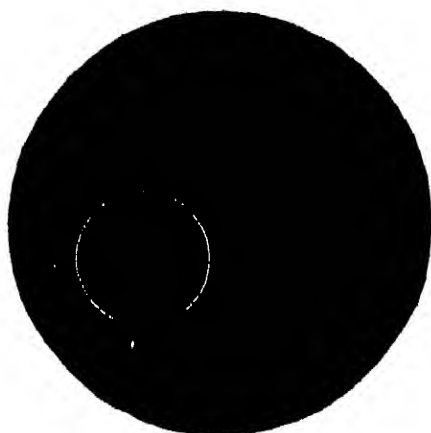


FIG. 47 (natural size).

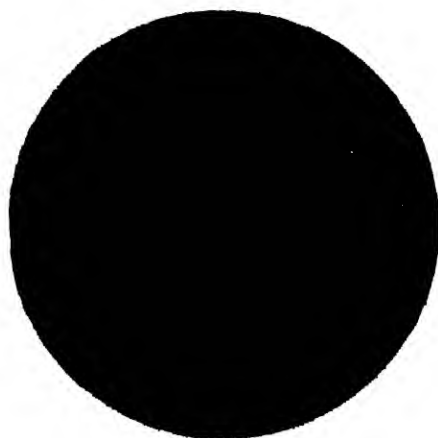


FIG. 48 (magnified).—Wrinkles formed on an over-thick coat of paint.

question, white lead covers better than zinc white. However, when the matter is approached from the point of view of the *weight* of white lead required to cover a given surface, then it is found that the conditions are reversed, *i.e.*, a given

superficial area requires a relatively greater *weight* of white lead but a greater relative *volume* of zinc white to become thoroughly covered. The covering power does not stand in a fixed ratio to the consumption of oil or varnish by the pigment: although good covering power is usually accompanied by a high capacity for absorbing oil or varnish.

#### NUMBER OF COATS OF OIL PAINT.

The question of *how many coats of oil paint must be applied to iron in order to ensure efficient protection against rusting*, and to prevent the passage of water or moisture through the paint itself, has really no connection with the covering power of the latter. For the mere covering of the substratum, two coats, in addition to the bottoming coat, will suffice in most cases; even one will in some cases be enough when the paint covers particularly well, though in such event the desired protection will not be secured. If it be desired to establish a standard number of coats of paint for this purpose, preference must undoubtedly be accorded to the paints requiring a large proportion of varnish to become properly workable, since it is really the varnish that has mainly to be considered, the pigment being taken into account only because too many coats would be needed if the varnish were used alone, and because, moreover, it is desired to give the object a different colour to that which it possesses naturally. It may be laid down as a normal standard that with a good paint one bottoming coat and three subsequent coatings, laid on at suitable intervals, will be required to produce a layer of oil paint of sufficient thickness on iron to keep moisture away from the metal and to protect the latter from rust for a reasonable time. There is no damage to fear from a larger number of coats, provided a sufficient interval be allowed to elapse after each coat before applying the next, since the individual layers will coalesce properly, and the

greater the total thickness the greater the degree of impermeability secured. That a different effect will result from laying the paint on too thickly has been already emphasised. The greater the number of strata of paint the longer will it take before the whole is destroyed and water can gain an entrance, therefore the longer will the iron remain free from rust. Formerly, in order to prolong the impermeability of the paint and the preservation of the coating, a practice was adopted which is now probably, owing to the expense, discarded, *viz.*, coating the incipiently decaying paint with a layer of linseed varnish. As we have already seen, the paint in course of time loses its lustre, the resinified linseed varnish continuously undergoing further changes, and the paint becoming absorbent towards liquids. If now a coat of linseed varnish be applied to the paint it is greedily absorbed by the latter, the interstitial spaces are filled up, the paint is impregnated with varnish and is able to resist further influence of the air for an additional period. Nowadays it is the custom to wait until the paint has become permeable and rust formation has begun, a fresh coat of paint being then applied, at far greater expense!

Another feature essential to the production of a good paint for preserving iron from rust is that the paint should be finely ground. When this is effected every minute particle of pigment will be thoroughly impregnated with oil or varnish, the whole forming a perfectly homogeneous mass in which no granules or the like will be found. If, however, the pigment, though in ever so fine a state of division, be merely stirred into the vehicle, without grinding, it will remain granular or gritty, and the granules will be apparent to the naked eye when the paint has been laid on; these irregularly impregnated particles of pigment being able to absorb moisture and facilitate its admission to the surface of the metal.

Paints that have either been insufficiently ground or not

ground at all—a condition often occurring with red lead paints for bottoming—are apt to curdle or separate into the constituent pigment and vehicle, the result being an uneven surface. Similar irregularities of surface are, however, noticeable in the case of many well-ground paints, particularly those containing specular-iron or micaceous-iron pigments. It is, however, desirable to secure as smooth a surface as possible, not only for the sake of the improved appearance but also since it affords fewer points of attack for atmospheric influences.

The circumstances to be considered in painting on iron have now been elucidated, and a number of conditions stated on which the durability of the paint depends. It has also been mentioned that every paint undergoes continuous alteration through oxidation, *i.e.*, by the absorption of atmospheric oxygen; and that under certain circumstances the pigment may contribute to accelerate this oxidation. That drying is purely a process of oxidation was demonstrated by Mulder, in his admirable work, he having determined the increase in weight by direct experiment. This has also been verified later by Spennrath, in a series of investigations wherein thin sheets of tin plate, 4 ins.  $\times$  8 ins. in size and of known weight, were coated with pure boiled linseed oil, whilst others were painted over with mixtures of linseed oil and various pigments. The whole series of plates were weighed on a delicate balance immediately after painting, and again when the coatings were properly dry; the increase in weight during drying averaging 13 to 14 per cent. of the weight of oil present. To determine the latter factor with precision the oil and pigment were accurately weighed before mixing; and, as the paint was laid on immediately after this latter operation had been performed, it is presumable that the ratio of pigment to varnish in the paint used was the same as that taken—an assumption confirmed by the slight divergences (less than 1 per

cent.) in the increases in weight observed. The author does not, however, unconditionally agree with Spennrath's further assertion that the gain in weight of the oil in a paint is a constant factor, and that this is a proof that the oil alone alters in drying, the deduction being that no chemical combination occurs between the oil and the pigment. In the case of lead paints, for instance, the pigment undoubtedly exerts an influence on the oil, otherwise the paint would not harden so rapidly as it does, for instance a red lead putty will set "stone hard" in a few days. Were no action on the oil to take place, the putty would necessarily remain as soft and plastic as that prepared from oil and graphite. Inert pigments, of course, have no influence on the oil.

In the course of his experiments upon rust prevention, Spennrath also turned his attention to whether some oil paints may be capable of exerting an injurious influence on iron; he came to the conclusion that in no case can an unfavourable effect be produced, for the simple reason that in all carefully manufactured paints the fine particles of the pigmentary substance are so well enveloped with varnish or oil as to prevent their coming into direct contact with the metal. This fact will scarcely be impugned, and so long as the oil or varnish is not completely decomposed, but still remains coherent, there cannot be any question of such action.

Other researches of Spennrath's related to the effect of different materials on the oil, and for this purpose he selected graphite as the pigment employed, in view of its perfect neutrality. In this connection he reports as follows: "It is not *prima facie* justifiable to assume, when rust begins to show itself on a painted iron surface, that the paint has suffered damage or destruction through the rust-forming agent. However carefully a paint may have been manufactured, one is never absolutely certain that the protecting coat is entirely free from microscopic holes, through

which the rust-forming agency gains access to the iron. As soon, however, as the smallest particle of rust has formed, the destruction of the coat of paint proceeds rapidly, simply because the rust spreads under the covering and causes it to separate from the metal. Moreover, there are certain injurious influences which attack the paint without, however, giving rise to rust. These may easily lead one to form erroneous conclusions if the occurrence or absence of rust should be regarded as the sole indication of the durability of the paint. It is altogether incorrect to consider the most active rust-forming influences as being always the most destructive to paint. For example, the resisting power of paint is often tested by immersing the painted iron object in a solution of common salt (brine); whereas in reality the test affords no criterion of this property, since, although brine rapidly produces rust, it is almost entirely devoid of influence on oil paint. On the other hand, if the painted iron does not rust under this test, all that is proved is that the paint is impermeable; if, however, the iron were exposed to other influences capable of corroding the paint, it would soon rust, on account of the metal being exposed."

Spennrath prepared a number of paint films by applying to sheet zinc a coating of boiled linseed oil mixed with graphite, and then dissolving away the metal by means of dilute sulphuric acid, which left the films of paint behind uninjured. These he stored for a certain number of months in (1) rain water, (2) sea water, (3) brine, (4) 10 per cent. sal ammoniac (ammonium chloride) solution, (5) 10 per cent. magnesium chloride solution, (6) 5 per cent. sulphuric acid, (7) 5 per cent. hydrochloric acid, (8) 5 per cent. nitric acid, (9) over acetic acid, (10) natural sea water in a closed chamber, (11) over dry calcium chloride, (12) aqueous extract of coal ashes, etc. The conclusions at which he arrived, from the changes induced in the films, are given below :—

"1. All oil paints are destroyed by dilute hydrochloric acid and nitric acid, gaseous hydrochloric acid, nitric acid, sulphurous acid (sulphur dioxide), and acetic acid. Dilute sulphuric acid does not corrode these paints.

"2. Caustic alkalis, alkaline liquids and gases, ammonia, ammonium sulphide, and soda solution quickly destroy any oil paint.

"3. Pure water exerts a more powerful rusting action than the generally dreaded solutions of common salt, sal ammoniac and magnesium chloride, and is even more active than natural sea water. The salt-content reduces the influence of the water, and the destructive effects observed in the case of sea water must be attributed to the mechanical action of the moving water on the coat of paint.

"4. Hot water is more speedily destructive than water at the ordinary temperature, and therefore destroys paint in a short time."

From the foregoing observations it results that none of the paints having a drying oil as a basis is capable of withstanding the continuous and prolonged action of acids, alkaline liquids, or even of water; and of course the same applies to the action of the fumes of coal smoke. Hence in this direction the question of rust prevention still remains far from being solved. This is a well-known fact, and no reliance is to be placed on the assurances of manufacturers that they can supply paint preparations capable of resisting all kinds of influences over a long period.

Spennrath made further experiments, investigating the influence of heat on the layer of paint, with the following result:—

"If a film of paint be exposed to a temperature of about 100° C., it undergoes considerable alteration in a short time, losing its elasticity and suppleness, becoming hard and brittle, breaking when folded over, besides losing in weight and

shrinking very considerably. These alterations also occur, though more slowly, at lower temperatures—still above the

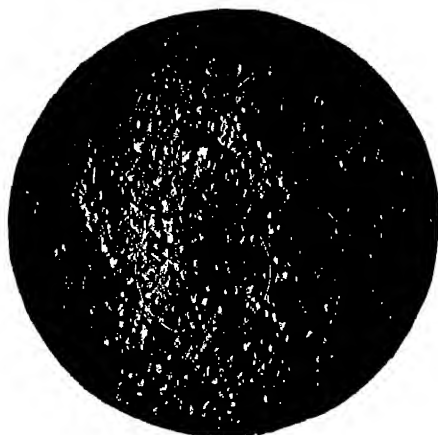


FIG. 49 (natural size).

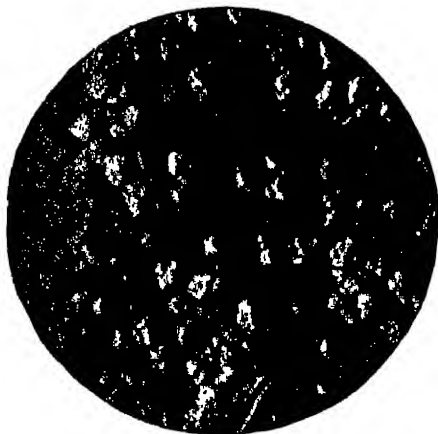


FIG. 50 (magnified).—Blisters and cracks caused by heating a layer of oil paint.

ordinary limit, while at 120° C. the film very soon becomes brittle like glass."

The conclusion drawn from these results is that "All paints suffer loss in weight by heat, and contract, thereby los-



ing their soft caoutchouc-like nature, and becoming stiff and brittle. So long as the film of paint remains attached to its substratum (iron) it cannot shrink, and a certain tension is therefore set up between the paint and the iron. The degree of tension increases with the increase of temperature and duration of exposure—especially in direct sunlight—and as the coating becomes at the same time more and more brittle it must finally tear, the result being the production of so-called air-cracks. These can be seen on all old paint, especially in paints on iron, intersecting the entire surface like a network, the exposed underlying metal being thereby delivered an easy prey to the action of rain ”

This conclusion is just as incorrect as is the approximation to natural wear in the experiment. A great difference exists between exposing to warmth a paint separated from its substratum, and subjecting it to the same conditions whilst still *in situ*; at least so the author has found, since he has been unable to confirm the alleged contraction and cracking of oil paint on iron through exposure, lasting several weeks, to a temperature up to 80° C. There is, moreover, an important difference between exposing paint to the ordinary maximum summer temperature and to a temperature of 100° C., to say nothing of the great difference in the influence of this last-named temperature on one side of a coat of paint as compared with its effect when exerted on both sides at once. All the deduction that can be drawn from these researches of Spennrath's is that the same effects are produced upon the paint by raising it to a temperature of 100° C. as are caused by an exposure to normal conditions over a long term of years, since in the latter case, also, the paint is brittle, hard, and cracked, or may be rubbed off in the state of powder. It accomplishes here in a short time the results otherwise taking years to produce—and no paint will last for ever.

There can be no doubt that in addition to the influences

already specified as capable of causing the premature destruction of paint, an electric current may also give rise to mechanical ruptures of the coating, caused by electrical discharges or shocks brought about in overcoming the resistance experienced by strong induction currents passing through iron structures; and finally, under certain circumstances, by galvanic action. Such ruptures consisting of fine cracks, or a loosening and perforation of the paint, being aided by the electrolytic decomposition of water, may result in a more rapid formation of rust than usual.

*Baking Paint on Steel Cars.*—After a large number of tests on small steel plates the Pennsylvania Railroad Co. in 1912 decided to build an oven large enough to bake the paint on a full-sized car; this was completed in January, 1913, and has been in continuous operation since then. The oven is 15 ft. high, 13 ft. wide, and 93 ft. 3 ins. long. It is lined with  $\frac{1}{8}$  in. steel shell and is covered with lagging 3 ins. thick, the lagging being held in position by an outer shell of galvanised iron. It is heated by steam coils, and is provided with a regulator for insuring an even temperature anywhere up to 275° F. The oven is provided with ventilators for admission of fresh air and for removal of the vapours which are evolved during the drying of the paint. The car is first covered with a priming coat inside and out which is baked on at 250° F.; it is then treated with putty where indentations occur and several covering coats are put on each of which is baked. The surface is then rubbed with emery cloth and oil to ensure a uniform surface and painted with two finishing coats of the desired colour. Lettering or decorations are then applied, after which a coat of varnish is put on to finish the operation. The use of such an oven results in much quicker work, the car not remaining in the shop so long as is the case when each coat of paint has to be dried at ordinary temperature; the work is much better done and the finish superior. The

results have been so far successful during the three years' running of this oven that two others are being built, and when these are finished it is probable that further extensions will be made.

*Painting Galvanised Iron and Tinsplate.*—In Circular No. 37 of the Educational Bureau of the Paint Manufacturers' Association, U.S.A., it is stated that the coating of zinc upon galvanised iron is not a permanent protection, the prevention of rusting being obtained at the expense of the zinc which gradually dissolves away. For this reason galvanised iron should be painted; but paint applied direct to galvanised iron does not adhere well, therefore it is advised to treat the metal first with a solution of sulphate, chloride, or acetate of copper containing 4 oz. of the salt to 1 gallon of water. This results in the deposition of a uniform coating of copper on the zinc which when dry exhibits a matt surface to which paints adhere very strongly. As protective paints, red white, and blue leads, zinc oxide, chromate pigments, and red and black oxides of iron are regarded as satisfactory. With regard to tinsplate which often rusts owing to the presence of pin holes and the cut edges, it is recommended to remove any palm oil left from the tinning process by means of benzine or turpentine and then coat with red oxide paint containing 10 per cent. of red lead, zinc oxide, or zinc chromate.

#### THE USE OF TAR FOR PAINTING ON IRON.

Although paints containing linseed oil or its derivative linseed varnish, have proved themselves the best of all protective media against rusting, it must be admitted that for many purposes oil paints cannot be employed, their cost being high and out of proportion to their durability. Among such purposes are: painting on iron pipes to be laid underground

on sheet-iron flues, on which oil paint would be carbonised ; on ordinary cast-iron articles, etc.

Nevertheless, it is undesirable to leave these objects unpainted, and hence use is made of coal tar, or, better still, a solution of coal-tar pitch in benzine or petroleum.

The coal tar used for this purpose must be purified from all constituents of an acid nature ; otherwise instead of the desired protection from rust, iron will, on the contrary, be even more readily rusted, since weak acids act on the metal and increase its tendency to oxidation. For this reason it is preferable to employ coal-tar pitch, the solid, neutral, resinous residue from the distillation of tar, converting it into paint by solution in benzine or petroleum ; in this case one is certain that the paint has no acid reaction. If the tar or dissolved pitch be carefully applied whilst hot, it forms an excellent and cheap protection against rusting, and at the same time imparts a deep black and fairly lustrous colour to the iron.

In respect to tar paints Spennrath expresses himself as follows :—

“ Tar paints were at one time largely used for the prevention of rust, but their employment has of late fallen into disrepute, the alleged protective action having been shown to be of very doubtful efficacy. It is true that a coating of tar is altogether insusceptible to the chemical influence of the atmosphere and also to acids and alkalis ; but, at the same time, the tar itself contains substances capable of causing iron to rust. Crude tar, for instance, always contains moisture, and, in addition to this, acetic acid is present in wood tar, the water and acid quickly causing the iron to rust. Hence it is that sometimes very extensive rusting can be detected—often to a considerable degree—under the tarry coating. Water-free or acid-free tar would not exert such action ; but the purification of the tar from these ad-

mixtures is troublesome, and increases the cost of this preparation, so that the advantages, as compared with oil paint, disappear. Finally, tar paints become softened by the sun's rays to such an extent that the mass runs and leaves the iron bare. Thus no security against rusting can ever be obtained by the use of tar paints.

"In point of resistance to external atmospheric influences, acids and alkalis, asphalt stands on the same footing as tar. True asphalt is, however, expensive, and has to be dissolved in a volatile medium before it can be used as paint. One preparation of this kind is the iron lacquer used more particularly for painting iron utensils for lavatory purposes. Being dear, and forming only a very thin protective coating, it cannot be employed for large surfaces and structures of iron.

"In the cold, asphalt is brittle, in consequence of which it easily cracks off and is speedily removed by the mechanical action of the dust carried about by air currents, rain and snow producing the same effect. I have found it impossible to preserve from rusting—even for six months—iron plates that have been painted with this material and left in the open air. Moreover, ordinary iron lacquer for the most part contains no true asphalt, but only hard tar, *i.e.*, tar pitch, which has the disadvantage of softening and running when exposed to the sun.

"Cast-iron water pipes and gas pipes are coated with tar or asphalt by dipping them in a hot state in the heated liquid material. This gives a staunch, strongly adherent coating, which, by reason of the high temperature at which it is produced, is also free from water. The pipes, laid in the ground, are protected from the action of heat; moreover, cast iron rusts far more slowly and with greater difficulty than wrought iron; in addition to which circumstances the rust itself—at the depth at which the pipes are laid underground—combines with the sand, etc., to form a protective coating.

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For example, the gas mains of the town of Aachen (Aix) when taken up, after lying in the ground for half a century, were found to be incrustated with a thick layer of siliceous rust, but in no case had any of the pipes become unfit for use; on the other hand, the house-service pipes of wrought iron were extensively corroded by rust in the upper portion. At present they are laid in asphalt, and I have myself examined such a pipe after five years' sojourn in its asphalt bed, and found it entirely free from rust."

Mulder makes the following observations on the use of tar as a protection against rust:—

"Tar is highly suitable for filling in the interstices of screws, nuts, and rivets, and will neither contribute to nor allow the formation of rust. Good varnishes prepared from constituents of coal tar are very slowly oxidised by the air, prevent oxidation by the empyreumatic oils they contain, and leave behind, on the volatilisation of these oils, a resinous layer, forming an efficient cover precluding access of air.

"One condition, however, is essential in such a varnish, *viz.*, it should never become quite hard. It will then never chip off under the influence of expansion produced by changes of temperature and the resulting friction of the surfaces of the connections, neither will it peel off through cold.

"In the case of large iron structures it is customary to connect adjoining surfaces by hot riveting, an operation which precludes the use of oil paint for the rivets. The same, however, does not apply to coal tar, which can here be used to advantage for coating the (previously cleaned) surfaces to be joined; and if the rivet holes be also brushed over with coal tar before the hot rivets are put in, no damage is done by the momentary charring of the tar, the residual matters between the plates and under the rivet heads being resin and carbon.



“Owing to the circumstance that oil paint will not adhere properly on coal tar (and *vice versa*) the objects to be afterwards painted must be freed from tar by scraping around the surfaces in contact before applying the permanent coat of paint, which must, however, be laid on with care in order that no openings for the admission of air or moisture may be left.”

#### DR. ANGUS SMITH'S METHOD OF TREATING IRON PIPES.

References are often made to Dr. Angus Smith's solution for preserving iron and steel. This is sometimes stated to be composed of coal-tar, rosin, pitch, and linseed oil, which are combined by heat, but it appears that it is not a solution but simply a method of treating iron and steel, more particularly water pipes, to prevent them rusting. For this purpose coal-tar is boiled to expel the water, ammoniacal liquor, and lighter oils, and the iron pipes, immediately after they have been removed from the moulds, and before any rust has had time to form, are heated to 300° F. and lowered into the prepared tar, then removed and allowed to drain.

## CHAPTER III.

### ANTI-CORROSIVE (RUST-PREVENTING) PAINTS.

*Conditions of Preparation and Application.*—Anti-corrosive or rust-preventing paints, the paints designed for preserving iron from rust and preventing the premature destruction of the metal, have attained to a position of great importance; and it is easy to understand that the industry concerned with the manufacture of such paints has attained very large proportions, many firms being now in a position to supply considerable quantities of such materials to railway companies and other large consumers. In order to increase sales it is alleged that some of these paints possess properties with which it is impossible for them to be endowed, simply because these properties can never be attained. When, for example, we read in a manufacturer's circular that he has invented and prepared a paint capable of destroying pre-existing rust, and thereby of preserving rusted iron from any further encroachment, it is evident, from what has been stated in the previous sections of this work, that such a claim is preposterous. If another maker avers that his product possesses magnetic or electrical properties, this serves no useful purpose, because a pigment ground up in, and therefore surrounded by, linseed oil or linseed varnish is thereby rendered altogether inert. Another manufacturer claims as an advantage for his paint that the pigment he uses, unlike those of others, does not undergo saponification with the oil in the varnish and therefore must be much more durable. It is, of course, well known that no saponification occurs in

paint, and that the durability of a paint may be reduced by the action of an oxidising pigment (red lead, white lead) on the oil or varnish, whereas an inert body exerts no action. Furthermore, in many instances totally unjustifiable claims are put forward on behalf of certain paints containing a pigment—iron oxide or graphite—in the form of scales or flakes quite visible to the naked eye. It is asserted that in these paints the individual flakes are completely enveloped in varnish and lie one above another in numerous strata so as actually to form a number of coats of paint in one. If, however, the scales be examined through a magnifying glass they will be apparent as a coarse, scaly powder ; but it will be found that the scales have for the most part disappeared, the field being occupied by coarse, angular fragments interspersed with a few lustrous plates. Now the author is convinced that, although these scales may, like finely pulverised pigments, be surrounded by the varnish with which they have been ground, it is altogether out of the question that there should be any superposition of scales—like fish scales—as alleged, since the paint is just like other paints when laid on, except that it forms a coating in which a magnifying glass shows the presence of a number of raised points representing the coarser particles of the pigment. He would, however, go still further, and say that if such scales actually do form the strata with which they are accredited, the same effect will be produced in still greater degree by the more finely powdered pigments, because the granules of the latter, being smaller, will lie closer together, forming a larger number of protective strata than the coarser particles can do. He therefore retains his previously expressed opinion that the scaly form exhibits no advantages over the finer powder of the pigments generally used, in either case taking a similar position in the paint, and the particles of both remaining enveloped in varnish or oil when the paint dries. The more

intimate, however, the connection between pigment and varnish, and the finer the condition of the paint, the longer will the latter discharge its functions. Nevertheless, the author has no desire to criticise any particular paints, and for that reason has not mentioned the articles by name.

Other advantages claimed for certain paints are power of resisting acid and insusceptibility to attack by alkalis.

Almost any oil paint, no matter what pigment it contains, will resist the action of dilute acid provided the exposure be merely a short one; otherwise it would be impossible to prepare a sample film of paint to demonstrate the acid-resisting properties of the same. Seeing that this is done by coating a thin sheet of zinc with the paint, and, after the coating is dry, dissolving the zinc by immersion in hydrochloric acid, thus leaving behind the film of paint, which thereby proves itself capable of resisting acid.

To be "acid-resisting," however, means to be capable of withstanding the continued influence of liquid or gaseous acids during several months, which is an impossibility. Even a 5 per cent. solution of hydrochloric acid will appreciably corrode a film of paint within three months, whilst 5 per cent. nitric acid destroys it at once leaving merely an unponderable residue. Moreover, no paint will resist the action of the smoky fumes evolved from coal fires, and it is therefore, as yet, impossible—all promises to the contrary notwithstanding—to provide a perfect protection for iron bridges and other structures exposed to such influences.

Alkalis exert a similar destructive action on paints, none of the latter being able to withstand continuous exposure thereto. It is true that one can wash paint over with a weak, or even a strong, solution of alkali without much injury, provided the surface be immediately rinsed with clean water; but continuous action—even only for a few hours in the case of strong solutions—is certain to bring about the complete destruction of the paint

The influence of water alone has already been considered. Paints cannot long withstand this when the immersion is continuous; for resisting water solutions of resin are far superior.

The effect of heat or fire on oil paints is in all cases destructive. This is a matter, however, that does not concern us much in dealing with paints for iron structures, and is only now referred to for the sake of completeness. No paint can withstand the direct action of flame, even old paints being first carbonised and then ignited, their destruction being thereby ensured.

The influence of temperatures between 70° and 100° C. on oil paint applied to iron is manifested in various ways, the paint either turning brown and finally black, though remaining otherwise intact; or else blistering, the blisters carbonising if the exposure should be prolonged. Blistering always ensues when the paint is suddenly exposed to strong heat (see Figs. 39 and 40). On the other hand a different effect is produced when the freshly applied paint is subjected to a moderate and progressively increasing temperature. Paint thus treated becomes unusually hard and firm, and will then stand even higher temperatures, up to 100° C. That paints of this kind constitute an ideal means for the preservation of ironwork has already been mentioned.

In addition to the unhappily increasing tendency to load the market with paints ostensibly endowed with impossible properties, there is an increasing sale of inferior grades of paint made from adulterated oil or pigment, or both. In the present age of reckless competition, as a general thing, cheapness is the first consideration—reliance being placed on the vendor's assurance that the paint is good; these adulterations are more frequent than is usually assumed; and, in spite of experience, it is difficult, if not impossible, to educate the public against the practice of placing orders with the seller

making the lowest tender. Apparently no thought is bestowed on the consideration that the contractor offering the lowest tender cannot honestly go below a certain limit of price, being obliged, like any other, to purchase his materials at a certain defined rate; and having to cover his expenses, which are far from small, must make up his deficit by employing adjuncts. The lowest offer often secures the order, and it is only after subsequent unsatisfactory experiences that the conclusion is arrived at that cheapness, in many and even in most cases, is synonymous with nastiness.

It is only in recent years that Railway Companies and Government and Municipal Departments, influenced by the unfavourable results obtained with bad paints and the dangers ensuing from the rusting of iron structures, have become enlightened, and now endeavour to secure the best paint by specifying normal standards and methods of testing the protective value of paints on ironwork. These endeavours are worthy of all recommendation and praise, and will certainly be productive of good, provided it be determined concurrently, as a fundamental rule, not to give the order to the contractor making the lowest tender; since he, knowing that the paint will be tested, may simply send in a few deliveries of good quality and then supply inferior stuff. As we shall see later, the methods of testing—especially for the oils used in paints—entail considerable difficulty and expense, so that it is very improbable that every cask of the paint supplied will be examined to see whether it is up to the standard. It appears that a better course would be to confide the orders to firms of known good standing, who can be relied on to adhere to the standards laid down, having nothing to fear if their products are put to the test; since, in spite of all precautions in the matter of testing, the unscrupulous maker will be sure to find a back door, and the consumer will have an unfavourable experience notwithstanding all his care.

Professor von Tetmayr of Zürich, President of the International Conference for the Establishment of Uniform Methods of Testing Building and Constructive Materials, made the following communication to the sub-committee appointed to deal with the testing of paints:—

“In order to obtain a basis for the establishment of a method of testing paints as preservatives of iron structures, it seemed necessary to review the current methods of testing anti-corrosive paints, and in particular to collect the requirements laid down in this respect in different countries.

“The results of the labours undertaken in this matter are, in one direction, of merely subordinate value for the simple reason that, notwithstanding the unfavourable experiences gained, the technology of the preservation of iron in iron structures has not received the consideration and attention required by the nature of the case. The great majority of technical men who have to deal with iron structures are more or less indifferent to the question of the means of preventing rust, frequently having no opinion on the matter; and up to the present scarcely anyone—in this age of copious advertisement—is able to distinguish the inferior from the really good article, or to make a correct selection of paint suitable for the purpose and local conditions in view. Good results obtained with individual paints are mostly a happy chance, and seldom the result of deliberation, or the exercise of a ripened expert judgment. The methods of testing the properties of paints have not yet emerged from their primitive condition; and where any examination is made at all it is confined to a few practical tests which generally extend no further than the determination of the drying power, the adhesive properties, toughness, and covering power. Experiments on a large scale are not lacking; and, indeed, are continually being repeated—in view of the prevailing uncertainty in the judging of the value claimed for

new paints—as an endeavour to replace existing kinds by better ones. The results obtained are not, however, as a rule made public, but remain the property of the officials concerned.

“The specified requirements exacted of rust-preventing paints in different quarters vary considerably in important particulars, as do also the results obtained with one and the same paint material. This divergence in results is by no means strange when the differences in the methods of treatment, and the external local influences, are considered; they merely offer a fresh confirmation of the old-established fact that nothing is universally good. Often causes and effects are confounded, as the decisions expressed on the suitability of red lead and iron oxide for bottoming paints clearly evidence. Thus, while in several countries, *e.g.*, France, Austria, etc., red lead alone is permitted, it is altogether banned in others. In the case of one of the principal Swiss railways, instead of employing red lead for bottoming, as was originally intended, the use of iron oxide was prescribed: presumably on account of an experience gained somewhere or other to the effect that rusted iron had been found under red lead paint. On the basis of this circumstance the dubious hypothesis of a surrender of oxygen by red lead to iron was invented, and consequently iron oxide was recommended. Moreover, it is well known that the same paint will vary in its behaviour in different places; in one, for example, it may last for six years and longer, whilst in another it requires renewal after only two or three years' service. To the expert there is nothing surprising in this variation; it will at most lead him to consider that, in the selection of the paint, no regard was paid to the adaptability of its chemico-physical properties to the local conditions; and that the event could have been foretold had a proper examination and appreciation of the prevailing conditions been made.



"As an additional experience may be cited the observation that similar paints may remain intact for different periods of time in one and the same situation, *i.e.*, under identical external conditions. In such cases it is evident that a variation in the composition of the constituent materials is in question; for this reason methods should be devised to facilitate the qualitative and quantitative detection of any substances present that may be capable of prejudicially influencing the durability of the paint."

*Composition of Anti-corrosive Paints.*

All paints for use on iron consist of a drying oil and one or more pigmentary substances, the whole being incorporated so as to form a workable paint. These are the fundamental constituents in every paint—even those with high-sounding special titles—the principal rôle in all cases being played by the drying oil employed as the vehicle. The oil usually employed is linseed oil, a vehicle which has been used for many years; it is cheap and obtainable everywhere; dries well (when properly prepared), and—when thoroughly dry—is unsurpassed in durability by any other drying oil. For general purposes neither poppy oil, nut oil, hemp oil, nor Bankul nut oil (all drying oils) is of any importance, as they are restricted to purely local use. Of late an addition to the drying oils employed in paint making has been made by the introduction of Chinese wood oil (varnish tree oil), and it is not impossible that when its properties, in particular its durability, have been thoroughly investigated, this oil may be found useful in the manufacture of protective paints. Its capacity for drying uniformly throughout appears to render it suitable for this purpose. On a later page a résumé of our knowledge concerning this oil will be given.

Landolt acknowledges good pigment and good oil as the principal conditions governing the quality of a paint; and if

these conditions are fulfilled a good result can be counted upon, provided the paint be properly applied.

Spennrath regards the oil paints as the most efficient preservatives against rust, but falls into error in assuming that the pigments employed have no influence on the durability of the vehicle. On the other hand, he is correct in his view that the pigmentary constituent of an oil paint may be selected in such a manner as to preclude the destruction of the paint from this cause. Concerning the injurious influences capable of attacking the vehicle, this authority asserts them to be incurable, and in this opinion also he is correct.

The following report on the practical tests carried out on the under side of a bridge in the Rue Lafayette, Paris, which is exposed in a special degree to the influence of smoke from locomotives, is furnished by Chief-Engineer Balat :—

The special paints were placed at disposal by their inventors or makers, whilst the ordinary paints used were prepared from chemically pure materials (red lead, white lead). The ten samples were applied, side by side, on the same sheets of metal, set at right angles over the railway track, so that each paint was exposed to the corrosive influence of the engine smoke under perfectly identical conditions. At the end of nine months the following results were obtained :—

*Sample 1.* One coating of linseed oil, one of red lead, two coats of grey, white-lead oil paint. This behaved well, the iron not being found exposed anywhere. Nevertheless, the presence of very small warty excrescences induces the supposition that the linseed oil coat had blistered, thus preventing the adherence of the red lead to the iron.

*Sample 2.* A coating of Anderghem iron-oxide paint and two coats of grey, white-lead oil paint stood the exposure well, and was found to be quite unaltered.

*Sample 3.* A double layer of a French "Panzerschuppen" (scale-armour) paint behaved well in the parts not directly

exposed to the action of the smoke; but in the centre the paint had suffered considerable corrosion.

*Sample 4.* A double coating with a blackish-grey composite paint of German origin was somewhat extensively corroded at the edges and in the centre.

*Sample 5.* A single coat of the last-named paint, covered by a layer of greyish-white paint from the same maker, was somewhat less affected than the preceding sample.

*Sample 6.* A single coat of a German blackish-grey composition paint, covered by a layer of brown varnish, was found to be greatly corroded over nearly the whole surface.

*Sample 7.* One coat of red lead, with a topping of tar and turpentine oil. This was found to have suffered greatly all over.

*Sample 8.* A single layer of red lead, and one of tar and turpentine oil. Highly corroded over the entire surface.

*Sample 9.* One coat of red lead and one of a French enamel paint. The latter had almost completely disappeared, leaving the red lead behind in fairly good condition.

*Sample 10.* A double coating with enamel paint. The paint had disappeared almost entirely. Extensive oxidation of the metal.

The deduction to be drawn from the foregoing results is that none of the new special paints possessed the properties claimed for them by the inventors. The tar paint is also useless; whilst the old paints, with a basis of red lead and white lead, still remain the best. It should, however, be remarked that red lead, which has been used by the railway company for the past few years, seems to be inferior in point of utility to iron oxide. This result is undoubtedly attributable to the linseed oil, with which the iron was first coated, having prevented the red lead from adhering properly.

Wiederhold expresses himself with regard to iron paints as follows:—

“By far the greater number of the compositions intended for preserving iron from rust are notoriously valueless, not a few being even injurious, and, in fact, up to the present, no substance has been discovered capable of adhering so firmly to iron under various atmospheric influences—and especially extensive fluctuations of temperature—as a good oil paint. Even in the comparatively limited number of instances where coating the iron with other metals less susceptible to oxidation could be advantageously effected, oil paint still remains the final resource whenever the metallic film (as in tinned and galvanised iron) disappears in the course of time. At the same time the present mode of coating iron with oil paints is not without its defects, and attention was recently drawn by Fairbairn—as the result of very unpleasant experience—to the fact that this means does not afford sufficient protection for the iron against atmospheric influences. This is especially the case where the metal is employed in the construction of ships and bridges, where consequently its preservation is of the highest importance; and it is consequently imperative that strenuous endeavours should be made to discover a more durable protective covering for iron.”

Toltz experimented with pure asphalt varnish, cheap grades of the same, lampblack, iron oxide, and graphite paints as coatings for iron, the tests extending to their resistance against heat and moisture. He proposes that “structures of iron, steel, and other metals should be carefully cleaned and then painted over with boiled linseed oil, or, better still, with a mixture of this oil and 10 per cent. of lampblack, asphalt varnish being also advisable as a first coating. They should be laid on thick and left for at least ten days to dry, a month being preferable. The best material for the second coating is graphite paint, which should contain at least 33 per cent. of pure graphite, but no turpentine oil, benzol, or driers. Parts of the structure exposed to vapours

and gases should receive a third coating with cheap asphalt varnish, as this will protect the underlying paints for years. Iron oxide paints are not very desirable for the first and second coats, graphite paint being preferable. When asphalt or lampblack paints are used, all trace of moisture should be previously removed, or the efficiency of the paint will be endangered. This precaution is less essential in the case of iron oxide and red lead paints, the linseed oil itself absorbing the moisture."

Against these views the following objections may be urged:—

In the first place, asphalt varnish cannot be used as a first coating for iron, since oil paints will not dry hard on this varnish, even after weeks have elapsed.

Secondly, the application of a thick primary coating is entirely opposed to the experience gained in practice, and is in fact inadmissible for the simple reason that thick layers of paint dry very slowly and wrinkle on the surface, whilst the underlying portions remain soft and are easily displaced.

Thirdly, painting should on no account be done on damp surfaces, and an absorption of moisture by linseed oil is entirely out of the question.

With the object of ascertaining the best means of most effectually preserving iron structures from rust, a North-American engineer, M. G. Huber, subjected a large number of old and new iron and steel bridges to a very careful scrutiny. From his communication it appears that in every instance rust spots were discovered under the paint. In many cases the extension of the spots was but slight, and the smoother the surface the less extensive the rusting, as a general rule; whilst iron plates were found to be less subject to attack than angle irons and girders. Similarly, pieces that had been heated to redness were found less susceptible to rusting, and the same was noticed in respect of all parts that

had been oiled in the workshop before being put into position and painted. As the investigations showed that the rust spots in older structures were not appreciably more extensive than in those of more recent date, Huber concludes that corrosion proceeds at a very slow rate. It is especially worthy of note that iron oxide paints appear to afford better protection than those made of red lead, the latter being very liable to peel and also easily detached from the underlying metal.

As the result of practical experience extending over a number of years, the author regards the following conditions as essential to the attainment of a durable anti-corrosive coating of paint on iron:—

1. The paint employed must be prepared in such a manner as to be easy of application, and form, when dry, a coherent layer possessing maximum powers of resistance.

2. In the absence of a better and more durable vehicle it should be prepared solely from pure linseed oil, free from extraneous admixtures, and contain none but practically inert pigments, ground as fine as possible. Pigments which impart any reaction, whether acid or alkaline, to water after digestion for twelve hours therein should be discarded from use. The practice of neutralising the acid reaction of linseed oil before grinding with the pigmentary substances is of no value, since experience has proved that the acidity reappears during the drying of the paint.

3. The paint should dry sufficiently in twelve hours to withstand any rainfall to which it may be exposed.

4. Grinding should be carried so far that no granules of pigment are left, the paint drying with a smooth surface, besides being easily distributable, and on no account liable to run down when applied to perpendicular surfaces.

5. The paint must not contain any turpentine oil, because this, in acting as a diluent, though rendering the paint more

workable, reduces the linseed oil ratio in the stratum paint.

6. The adhesion to the metal must be perfect, and dried paint must be elastic and remain so for a long time.

Simon lays down the following conditions to be fulfilled by a good paint for iron :—

1. It should afford a protective air-excluding cover over the iron.

2. The materials used in the paint should be free from bodies capable of attacking iron or liable to be decomposed by atmospheric influences.

3. In addition to high adhesive and cohesive properties the paint must be very elastic and have a coefficient of expansion approximately equal to that of iron.

4. In the selection of the materials regard must be paid to the question of conductivity in respect of heat and electricity. Hitherto these factors have been almost entirely neglected, although both are of importance.

5. The colour of the paint should be such that incipient rusting can be detected, and timely precautions taken to prevent more widespread corrosion.

All that is necessary to be said with regard to anti-corrosive paints, or the conditions under which they fulfil their *raison d'être*, having been discussed, attention will now be directed to a description of the component materials. It is sufficiently well known that linseed oil paints afford the best means of protection against rusting, and, in principle, the composition of any oil paint is very simple.

## CHAPTER IV.

### LINSEED VARNISH AND WOOD OIL.

Raw linseed oil is scarcely ever used as a varnish in practice, owing to its slow rate of drying, linseed varnish, incorporated with a finely divided pigmentary substance, forming the basis of the oil paints. On applying the paint to any surface it is distributed by the brush as a thin layer, which covers the underlying material, and, by absorbing oxygen from the air, dries to form an elastic coating highly adherent to the iron. That, under certain conditions, the pigment may exert a contributory action is not impossible; nevertheless it may be assumed in general that such is not the case, the pigment usually having no influence at all on the drying properties, being merely enveloped in the linseed varnish. In this way the pigment is completely protected from external influences; so that even where it is susceptible of decomposition—as is the case with zinc white, for example—destructive influences cannot come into play so long as the skin or cover of varnish remains intact. White lead, also, is decomposable by weak acids; yet no one would class white lead among the unstable pigments, since it is protected from external influences by the enveloping varnish and at the same time prevented from exercising any effect on the underlying metal, both contingencies being precluded until the varnish has suffered from corroding influences.

Thus we see that linseed varnish is the principal component of all paints; and in giving this fact due recognition



the Conference already mentioned propounded the following questions for discussion:—

1. What are the characteristic properties of a good linseed varnish?

2. What extraneous bodies are contained in the commercial article?

3. What admixtures are injurious and what innocuous with reference to the employment of the varnish in the preparation of paints for ironwork?

4. In which direction and by what methods should the varnish be examined with reference to the aforesaid object?

Before going more closely into the solution of these problems, it will be necessary to devote a few words to the preparation of the linseed varnish itself.

When linseed oil is heated, at first to a temperature of  $130^{\circ}\text{C}$  until all the contained moisture—which reveals itself by a copious production of bubbles—has been driven out and then afterwards to about  $270^{\circ}\text{C}$ . for three or four hours with an addition of so-called driers (lead and manganese compounds, such as red lead, litharge, sugar of lead, manganese peroxide, manganese borate, etc.), a quick drying but somewhat viscous varnish is obtained, which in all cases is thicker than the original oil, and up to about fifteen years back was the only kind classed as linseed varnish.

If, on the other hand, the oil be raised to a temperature of  $130^{\circ}\text{C}$ . as before, and one of the above-named substances or an oleate, or resinolate of lead or manganese, be then stirred in, an equally good drying but more fluid product will result. Such are most of the commercial linseed varnishes of the present day.

Besides these two kinds, which naturally differ chemically—the presumption being that the greater and more protracted heating to which the former class is exposed causes a more extensive alteration of the constituents

substances than when the oil is heated to merely  $130^{\circ}$  C., though no actual investigations have been made on this point—other linseed varnishes are met with in commerce, and consist of (a) linseed oil mixed with driers; or (b) linseed oil which by some special process is made so active that it surpasses the best boiled oils in drying properties, and, in addition to being more fluid, is endowed with an excellent lustre. In the author's opinion this product is a linseed oil of unaltered composition, and should be preferred to all linseed varnishes prepared in other ways.

The question now arises as to which of these four different classes of linseed varnish is the most suitable for ironwork. In this connection it may be stated that, so far as the author is aware, no attempts have been made to subject the four kinds of varnish in the form of paints to a practical test, side by side and under identical conditions, so as to enable a comparison to be made between them. This deficiency is due to the simple fact that, on the one hand, there has been no inducement to do so, and that, on the other, the deep-rooted belief that boiled linseed varnish is the sole kind worthy of the name has caused every varnish maker to launch his ware under the title of boiled varnish. The author was himself long an ardent supporter of boiled linseed varnishes, but has become convinced by a series of trials that linseed varnishes prepared at a temperature below  $270^{\circ}$  C. are at least not inferior to the boiled varnishes in so far as drying is concerned.

It would be of great interest in the solution of the problem now under consideration—namely, the relative value, as a coating for iron, of linseed varnishes prepared respectively by heating to  $270^{\circ}$  C.; by heating to  $130^{\circ}$  C.; by mixing with liquid driers, and by rendering active the unaltered oil—to have, in addition to an exhaustive chemical examination of the varnishes by competent persons, a practical test

of their efficiency carried out by some railway official. Of course in the latter tests an identity of pigments and conditions of use would be necessary to the attainment of reliable results. It is only by practical experiments on a large scale that the question can be settled, and not by following the example of Amsel, who, after having long denounced the addition of resinato compounds as an adulteration, all at once came to the surprising conclusion that the unboiled linseed varnishes prepared with metallic resinates are not only equal but superior to the boiled varnishes. The author, not being an analyst, is not in a position to investigate and determine the chemical differences presumably existing between the four classes of linseed varnish; but practical experience has induced the conviction that a linseed oil which has not been exposed to far-reaching dissociation through the influence of high temperatures must be more durable than one that has been so affected, even if only because practical experience teaches that linseed oil is much less rapidly decomposed by atmospheric influences than is the case with linseed varnishes prepared by strong heating.

The amount of driers employed in the manufacture of linseed varnishes varies, amounting to between  $2\frac{1}{2}$  and 8 per cent. in the case of lead compounds; 1 to  $2\frac{1}{2}$  per cent. of manganese compounds; and  $1\frac{1}{2}$  to 5 per cent. of metallic resinates. The temperature and duration of heating also vary—sufficient factors in the author's opinion to induce differences in the durability of various grades of even good and pure linseed varnish.

Now to consider the factors by which the necessary oxygen absorption, causative of drying, is influenced, bearing in mind that it is now recognised that the acceleration of drying is not due to the amount, or oxygen content, of the added driers, but that the object in view is to incorporate

with the oil substances capable of absorbing atmospheric oxygen with avidity and rapidly parting with it to the oil.

According to Livache, the main considerations regulating the increased absorption of oxygen by drying oils, such as linseed oil, are :—

1. The degree of purity of the oil itself.
2. The age of the oil.
3. The method of storage
4. The temperature (heat) employed.
5. The addition of certain substances.

1. *The Purity of the Oil*.—Every oil on issuing from the press is contaminated with water and other impurities, from which it must undoubtedly be freed before an elastic mass can be produced. This object is attained either in a natural manner by subsidence, or by filtration, or finally by chemical treatment. The latter method, which generally consists in an addition of sulphuric acid, results in the destruction of substances incapable of occluding free oxygen, and therefore having no influence on the drying of the oil. If freshly pressed linseed oil, and oil that has been treated with sulphuric acid, followed by washing until neutral, be exposed to the air, it will be found that the second oil takes up a larger quantity of oxygen than the first.

2. *Age of the Oil*.—Linseed oil stored in such a manner as to exclude air will subsequently absorb oxygen in amounts varying directly with the duration of such storage up to a limit.

3. *Method of Storage*.—If the oil is stored so that air can gain access, it will be found to have absorbed a certain quantity of oxygen during storage. Experience shows that this is slow to commence, but once initiated it proceeds rapidly, and will therefore be the farther advanced the longer the oil has been exposed to the air.

4. *Influence of Heat*.—The temperature at which an oil is

exposed to the action of the air has an influence upon its drying properties. It was demonstrated by Chevreul that linseed oil at a temperature of  $25^{\circ}$  to  $28^{\circ}$  C. dried quicker than at  $15^{\circ}$  to  $18^{\circ}$  C. If crude linseed oil and similar oil that has previously been heated are exposed to the air under identical conditions of temperature, the drying properties differ. Linseed oil that has been heated for three hours to a temperature at which merely a few separate bubbles of gas ascend to the surface, dries more rapidly than unheated oil and takes only half as long to set hard. Fahrion states that by such light boiling in deep vessels, so that access of oxygen is prevented, the modification of the unsaturated fatty acids is accelerated, and products are formed which are capable of rapidly absorbing oxygen. On the other hand Chevreul, who heated the oil under similar conditions, found that an oil heated for five hours dried less satisfactorily than one heated for only three hours. It is doubtful whether under the influence of protracted heating a portion of the glycerine is decomposed—as the odour of acrolein would imply—and consequently linolic acid is liberated; but it is known that this acid dries less quickly than linolein. For the same reasons it is also doubtful whether Mulder found linseed oil heated to  $60^{\circ}$  to  $100^{\circ}$  C. dry less satisfactorily than raw oil. On this point it may be said that:—

(a) A moderately high temperature improves the drying power of raw linseed oil; and

(b) A linseed oil exposed merely to such a temperature dries less rapidly than one that has been previously subjected to the influence of heat; but only provided the heat employed was not so great as to cause incipient decomposition of the oil accompanied by the formation of a certain quantity of linolic acid.

5. *Addition of Certain Substances.*—It has long been

known from experience that the addition of certain substances, such as white lead, litharge, manganese oxide, etc., increases the drying properties of the drying oils.

In certain cases these substances are mixed with the oil in the cold; whilst in others the oil and driers are brought together while under the influence of heat. To take, in the first place, the lead compounds, which have long been in use, the general practice is to heat the oil with the lead drier, the latter being added at the stage when linolic acid has been liberated through the action of the heat employed. Hereupon the oil becomes oxidised by the oxygen in the lead oxide, and when the operation is terminated a certain amount of metallic lead is found in the residue.

This double reaction is apparently without influence on the resulting effect: in the first place, experience teaches that lead linolate does not impart any actual drying properties, being pulverulent; and, in the second place, linolic acid dries less rapidly than linolein. Nevertheless it is indisputable that a linseed oil heated along with lead oxide possesses greater drying powers than a raw oil or one boiled without addition of such oxide. However, when it is remembered that a good linseed oil, exposed to the air, absorbs oxygen to the extent of 16 to 18 per cent. of its own weight in undergoing conversion into a solid mass; and when, moreover, it is recollected that the quantity of lead oxide (red lead, or litharge) used does not exceed in practice 3 to 8 per cent. as a maximum; it will be evident that the above quantity of oxygen cannot be supplied by the lead oxide, since the amount present in the latter is only about 1 per cent. as compared with the 18 per cent. required. Consequently such addition of lead oxide can only play a small part in the oxidation of the oil. Moreover, some portions of the lead oxide do not sustain any loss of oxygen, the oxide combining with the oil to form a lead soap. Nevertheless, the presence of a

certain quantity of metallic lead at the end of the oxidation process proves that the oxide has, to a corresponding extent, participated in the work of oxidation; and we have seen, from the influence of oxygen on the raw oil, that the drying power increases when the oxidation of the oil has attained a certain degree.

Similar observations and deductions have been made in connection with the drying powers when manganese compounds are employed. An appropriate explanation is, however, afforded by the important observation recorded by Chevreul, to the effect that when linseed oil is applied to a bright surface of metallic lead, free from any film of oxide, a considerable increase in the drying power of the oil is noticeable. Here it is indisputable that the oil could not have absorbed oxygen from any other source than the atmosphere, and it is therefore solely the presence of the metal that has increased the drying power of the oil.

This fact may, however, be followed up still further. If a raw drying oil be mixed in a flask with porous lead obtained by decomposing a lead salt with some other metal, the drying properties of the oil are greatly improved, without any elevation of temperature. In this case the possibility of any absorption of oxygen by the oil is altogether precluded. It therefore follows that a small amount of lead dissolved in the oil (acids) is sufficient to increase the drying power.

In the case of manganese compounds this drying power cannot be proved directly. Lead, however, can be replaced in the oil by manganese, it being sufficient to treat the oil—previously treated with lead—with a manganese salt, such, for example, as manganese sulphate; whereupon double decomposition ensues, an insoluble lead salt being formed, whilst the lead in solution in the oil is displaced by the manganese. The drying properties of oil treated in this manner are high, and far superior to those of oils boiled with

manganese salts. This circumstance may be explained as follows: when the oil is spread out in a thin layer so as to facilitate access of air the film assumes a dark colour owing to the manganese oxide being raised to a higher state of oxidation by the oxygen of the air; afterwards, in proportion as the oil thickens and dries, this dark coloration progressively diminishes, the oxidation of the manganese peroxide having thus been the means of oxidising the oil, so that finally a solid and perfectly colourless mass is obtained.

The aforesaid coloration and subsequent complete decoloration show that the manganese oxide has served as a carrier of oxygen, itself taking up oxygen from the air and then parting with it to the oil. In the case of lead oxide the process is probably the same, though less energetic.

Hence lead or manganese compounds used as driers in oils play an intermediary part, yielding up their absorbed atmospheric oxygen to the oil, and thus rendering the latter quicker drying than it would be without their assistance. The natural sequel to this discovery is to endeavour to ascertain whether the same *rôle* of intermediary is played by metals other than manganese and lead; the simplest way of testing this being to take oil that has been boiled with litharge and add to it a metallic salt containing an acid which forms with lead a compound insoluble in oil. As we have already seen, oil heated with litharge and spread out thin will dry in twenty-four hours. However, on replacing the lead in the oil by copper, zinc, or cobalt, the oil does not dry in thirty-six hours; and when nickel, iron, chromium, etc., are substituted in the same way the drying is protracted to forty-eight hours. The observation that oils from which lead has been displaced by manganese dry more rapidly than those prepared with manganese salts direct is very important. Industrially, certain preparations of lead or manganese are used,



but their selection is apparently regulated by their ratio of solubility in the oil when heated, and consequently preference is given to lead acetate and manganese borate, both of which are decomposed by heat, yielding up to the oil lead oxide and manganese oxide respectively, the beneficial influence of these oxides being well known.

On heating lead acetate to about  $100^{\circ}\text{C}$ . it parts with its water of crystallisation, in which it melts at  $75^{\circ}\text{C}$ ., and also with a little of its acetic acid; if, however, the heat be increased to  $280^{\circ}\text{C}$ ., the salt decomposes altogether into lead carbonate, leaving behind as a residue finely divided lead, which plays the chief part in the drying of the oil. Like all the other manganese compounds, manganese borate is of a somewhat unstable nature; the affinity of boric acid for manganese oxide being very slight, the acid is easily set at liberty on the application of heat. Hence the only advantage resulting from the use of this salt is the readiness with which its manganese oxide can be introduced into the oil.

As already remarked, unoxidised lead in a highly porous condition has a very important influence on the drying power of the oil; it is also of interest to learn the effect of other metals readily obtainable by precipitation. Only a very slight accession of drying power is found to result, however, from the use of precipitated copper or zinc; this might have been presumed from Chevreuil's observation that linseed oil, applied to lead free from oxide, dries much quicker than on sheets of copper, zinc or iron, the latter metals having no action, the oil drying thereon as slowly as on glass or porcelain.

So far as the numerous substances, other than lead or manganese compounds, that have been from time to time proposed as driers are concerned, none have any appreciable effect. Chevreuil showed that so far from increasing the

drying properties of oils, some of these substances—notably antimony salts—produce quite the opposite result. Even when a favourable influence has been found, exceptionally, to follow the use of individual salts, it is in reality attributable solely to the heat employed.

According to Simon it still remains to be proved whether the *ozonised linseed varnish* recently placed upon the market is really deserving of notice. If ozone be passed through oil, only a part will enter into chemical combination, by far the greater proportion being simply absorbed and retained on account of the affinity for gases displayed by oil. Proof that a large quantity of uncombined oxygen is present is afforded by the circumstance that oil treated in this manner gives no reaction with zinc iodide and starch, though when heat is applied a blue coloration is developed. It is thus scientifically demonstrated that an available supply of oxygen is present, which might be a source of danger liable to cause rusting in case moisture and carbon dioxide obtained access.

#### *Properties of a Good Linseed Varnish.*

The author, deeming it necessary to go fully into details to make the subject generally comprehensible, will now deal with the first point arising in this connection, *viz.*, the characteristic properties of good linseed varnish.

Landolt discusses the matter as follows: "By normal, *i.e.*, pure, linseed varnish we understand solely the product obtained by boiling or heating pure linseed oil to temperatures between 180° and 250° C., with, perhaps, the addition of some drier. The specific gravity at 15° C. and viscosity at 20° C. should be determined.

"Pure, good linseed varnish ought to be clear, pale to dark yellow in colour—according to the heat and driers employed—and should dry, dust-proof, within twenty-four hours at the outside. The consistency is somewhat thicker than

that of raw oil: viscosity should be determined in round numbers, probably at 20° C. The taste and smell are more or less characteristic to an expert."

The author long ago stated the characteristic properties of a good linseed varnish, in the following terms:—

*Consistency*.—A good varnish must be somewhat more viscous than linseed oil, but not so viscous as to require reducing with turpentine to make it workable as a paint, otherwise it would produce too thick a coating—the drying would then be merely superficial and the paint would be liable to crack.

*Colour*.—This varies according to the method of preparation adopted, but should usually be pale yellow to reddish-yellow, or even reddish-brown, but on no account dark brown or blackish-brown.

Varnishes prepared by steam heat are paler than those boiled over direct fire; and manganese varnishes—*i.e.*, those in which manganous borate or manganese hydrate is used as a drier—are paler than those prepared with lead acetate, litharge, red lead, manganese dioxide, etc., approaching in fact more nearly in this respect to the varnishes produced by the aid of atmospheric air or by the direct introduction of oxygen gas. The duration of heating also exerts an influence on the colour, the longer the exposure to a high temperature the darker the varnish, by reason of the partial carbonisation of colouring matter, etc., and the consequent brown coloration they impart.

*Smell*.—The odour of a good varnish resembles that of linseed oil, but accompanied by a slight empyreumatic aroma like that of the vapours evolved on heating; it may be unpleasant, but should not be bad, or still less resemble the smell of fish oil or rosin oil, which would indicate the presence of these bodies as adulterants. If overheated the varnish will

possess a disagreeable empyreumatic smell, and be blackish-brown in colour.

*Flavour.*—This also resembles that of linseed oil, but is more irritating, bitter, and unpleasant. The flavour affords the quickest and readiest means of detecting adulterations with fish oil and rosin oil.

Good linseed varnish must neither be turbid nor contain solid matter in suspension. If not clear it should be left in complete repose for at least fourteen days in a moderately warm situation, at the end of which time it will, if free from rosin oil, have become clear, and the amount of sediment deposited will enable one to readily determine whether the varnish had already been clarified or not. Every varnish, no matter how well treated in this respect, will form a slight deposit during prolonged storage, but even after some months this should not exceed  $\frac{1}{4}$  per cent., and is therefore negligible.

Many varnish makers carry out the clarifying process in a very perfunctory manner, sending their products out almost as soon as made, the consequence being they reach the consumer in a turbid condition and require a fortnight or a month to become bright; the sediment may amount to as much as 7 per cent., and to say the least such goods may be considered as imperfect.

*Drying power* is one of the main characteristics of good linseed varnish; when spread out in thin layers, without any addition of pigmentary substances, on glass or metal, it should be so far dry at the end of twenty-four hours as to afford no hold to dust, etc., *i.e.*, not tacky, and be set hard within another twenty-four hours, whilst still, however, retaining a certain degree of elasticity and flexibility. Should it dry quicker it would be in some respects an advantage; but if on the other hand it dries more slowly, this is an indication that it has been insufficiently boiled, contains too small a proportion of driers, or has been adulterated.

With regard to the nature of the extraneous matters (adulterants, etc.) present in the commercial article, and as to which of these are inimical and which harmless in view of the employment of the varnish in the preparation of paints for ironwork, Dr. A. Landolt divides the adulterants present in commercial linseed varnish into two kinds—*intentional* and *accidental*.—

“ The intentional admixtures (*i.e.*, adulterants) are : rosin (colophony), rosin oil, raw (unboiled) linseed oil ; petroleum residues of high boiling-point, and mineral oils. The varnish prepared by the so-called cold process must also be regarded as a falsification, since this product is unsuitable for use on ironwork. The previously mentioned adulterations with fish oil, tallow, camelina oil, poppy oil, hemp oil, etc., are rarely, if ever, practised, linseed oil being as a rule cheaper than any of these oils. The principal adulterants are rosin, rosin oil, raw linseed oil, and mineral oil.

“ First place among the accidental adulterants may be accorded to the suspended impurities which render the varnish turbid, the second place being occupied by water, derived from damp casks. The injurious admixtures are rosin, rosin oil, and non-drying oils, as well as the linseed varnish prepared by the cold process, and raw oil.”

No proper distinction can really be drawn between injurious and harmless admixtures in linseed varnish, since all those in question in the adulteration of the varnish—such as rosin, rosin oil, mineral oil, and substitutes—exercise an unfavourable influence on the drying, hardening, and durability of the paint. Even accidental moisture is injurious, in so far that it at least retards drying and hardening, which retardation constitutes the first appreciable difference between pure and adulterated varnish, and one that is attended by unfortunate results. Linseed varnishes adulterated with rosin oil and rosin dry more slowly than when pure, and also harden more

slowly, or not at all, in the latter event remaining soft and tacky. Moreover it is found that such adulterated varnishes, though at first apparently dry and hard to the touch, become tacky again after a lapse of some weeks, and thus allow dust to adhere and form a solid crust on the surface. It is also well known that they are very liable to crack after a while. Mineral oils also retard drying and prevent the paint from setting hard. If present in appreciable proportions they also give rise to the remarkable phenomenon of a separation of the linseed varnish from the mineral oil, the former drying under a superficial layer of the latter, which remains indefinitely in its original liquid condition.

With regard to the methods by which varnish should be tested, with a view to ascertain its suitability for use in paints, the investigation of the drying oils or linseed varnishes has, after a long period of neglect, made some progress during the last few years; the director of the experimental department of the German Painters' Association in Kiel, Dr. Amsel, has greatly interested himself in the matter, and has published his results in numerous pamphlets and the technical press. Without going more closely into these results or their reliability, the author will at present merely refer to one method, the so-called water reaction, which is claimed to detect in a simple manner various specified adulterations. It would considerably exceed the limits of the present work to quote all the interesting details of the various treatises by Dr. Amsel, but it is sufficient to mention that they may be found in the *Berichte* of the German Chemical Society (1897). Amsel's views have given rise to the publication of various conflicting expressions of opinion by other chemists, such as Dr. Lippert and Dr. Weger; and as the question is by no means finally settled, the author considers it advisable to refrain from reproducing such controversial matter, but will content himself with devoting attention to the ordinary

methods of examination, merely giving the reference where the others may be found.

The methods of testing arrange themselves naturally into two groups: A - physical and chemical tests: and B—so-called practical or empirical tests.

Under group A are to be classified—

1. Specific gravity.
2. Viscosity at 20° C.
3. Refractive index
4. Setting or solidifying-point.
5. Melting and setting-points of the fatty acids.
6. Saponification value.
7. Iodine value.

8. Detection of rosin, rosin oil, raw linseed oil, linseed oil substitutes, mineral oils.

9. Determination of the added driers.

B. The practical or empirical tests relate to—

1. Brightness.
2. Taste and smell.
3. Behaviour on heating to 300° to 320° C.
4. Drying power.

The constants for raw linseed oil given by Tiewkowitsch are as follows:—

Specific gravity at 15° C.	. . . . .	0.931 to 0.911
Solidifying-point	. . . . .	- 26° C.
Melting point	. . . . .	- 16° to - 20° C.
Saponification value	. . . . .	190.2 „ 195.2
Iodine value	. . . . .	170 „ 206.4
Refractive index at 20° C.	. . . . .	1.4800 „ 1.4812
Holmer value	. . . . .	94.81 „ 95.6

The insoluble fatty acids had the following characters:—

Specific gravity at 15.5° C.	. . . . .	0.9233
Solidifying-point	. . . . .	13.3° to 17° C.
Melting-point	. . . . .	17° „ 24° C.
Neutralisation value	. . . . .	196 „ 198.8
Mean molecular weight	. . . . .	283
Iodine value	. . . . .	179 to 200.8
Refractive index	. . . . .	1.4646

The United States Government issued the following specifications for linseed oil in August, 1912:—

“The oil must be strictly pure, well-settled linseed oil, perfectly clear, and not show any deposits of ‘foots’ or a loss of more than 0·2 per cent. when heated for one half-hour to a temperature of from 103° to 105° C., it must show on examination the following characters.—

	<i>Maximum.</i>	<i>Minimum.</i>
Specific gravity at 15° C. . . . .	0·986	0·982
Specific gravity at 25° C. . . . .	0·981	0·927
Iodine value (Hanus) . . . . .	190	178
Saponification value . . . . .	192	189
Acid value . . . . .	8	—
Refractive index at 25° C. . . . .	1·4805	1·479
Unsaponifiable matter per cent. . . . .	1 5	—

“The oil when poured on a glass plate and allowed to drain and dry in a vertical position, guarded from dust and exposure to weather, must dry free from tackiness in less than seventy-five hours at a temperature of from 15·5° to 26·5°.”

The behaviour of the varnish when heated to 300° to 320° C. affords important indications. Good, pure linseed varnish should remain clear under this treatment without coagulating or becoming “lumpy,” as the technical term has it, *i.e.*, it should not form any gelatinous excretions.

Landolt says: “The so-called commercial linseed oil, which is the sole quality coming under consideration, is rarely free from watery and mucilaginous substances. From these it can be freed to a considerable extent by prolonged storage in suitable vessels. In ordinary commercial linseed oil, however, it will be seen that, as soon as the temperature reaches 175° C., a number of bubbles form at the surface, and, after a short time, coagulation sets in owing to the formation of lumps which rise and fall in the liquid, frequently collecting into conglomerations resembling frog spawn. In this manner the oil may be freed from these injurious accessory consti-



tuents, and consequently every good linseed varnish should be heated to this temperature unless an oil clarified in a superior manner by storage is used.

"These substances are still present in a dissolved condition in linseed varnish prepared by the cold process. This varnish becomes lumpy when heated, while oil or varnish of normal constitution, free from these substances, never does.

"The drying power is ascertained by spreading the varnish out on glass plates. Good linseed varnish should dry dust-proof, within twenty-four hours, at a temperature of 15° C."

#### *Adulteration with Rosin.*

Varnish adulterated with rosin is more viscous than usual; dries in thirty-six to forty-eight hours; is apparently solid, but becomes tacky at the temperature of the hand—tested by laying the hand on the painted surface. Dust will readily adhere to paint made from such varnish which it renders grey and dull in appearance. After a brief exposure to the weather the paint perishes and falls off.

If linseed varnish, in which an adulteration with rosin is suspected, be shaken up frequently during several hours with strong (95 per cent.) alcohol, then left at rest and the resulting extract decanted, the adulterant may be detected in the latter. To this end the extract is distilled in a flask connected to a condenser and receiver, or in a distilling apparatus, the recovered alcohol and undistilled residue being weighed. If the latter exceed  $\frac{1}{16}$  part of the alcohol taken falsification with rosin or rosin oil is revealed, because only 1 part of linseed oil or varnish is soluble in 40 parts of alcohol.

When varnish adulterated with rosin is exposed in a flat vessel to the action of the air, a portion of the rosin will separate out, in ten to fourteen days' time, in small crystalline granules which can be readily identified as such.

A more circumstantial method of detecting the presence

of rosin is to boil the varnish for a few minutes with 95 per cent. alcohol, drawing off the solution when cool and then treating it with lead acetate solution. In the case of pure varnish merely a slight turbidity is produced, whilst if rosin be present, a lumpy white precipitate is formed, which can be converted into pure rosin by repeated washing and melting.

#### *The Detection of Unboiled Linseed Oil.*

The detection of unboiled linseed oil in varnish is based on the percentage content of unaltered glycerine. To determine this, 5 grams of the oil under examination are saponified in the usual manner, and the soap decomposed by hydrochloric acid; whereupon, after standing a little while, the acid liquor containing the glycerine is filtered away from the insoluble fatty acids. The glycerine solution is rendered strongly alkaline by caustic alkali, and then treated with crystals of potassium permanganate until the liquid assumes a persistent pale red colour. A little sodium sulphate is then added to decompose the excess of permanganate, the manganese oxide is removed by filtration, and the filtrate heated to boiling after acidification with acetic acid, the solution being finally decomposed by calcium chloride. The formation of a white precipitate of calcium oxalate indicates the presence of glycerine. This contains some silica, it is therefore ignited to  $\text{CaO}$  which is dissolved in a measured excess of half-normal hydrochloric acid and titrated back with half-normal caustic soda, 80 parts of  $\text{NaHO}$  equals 92 parts of glycerol.

#### *Adulteration with Fish Oil.*

Adulteration with fish oil can be detected by the taste and smell, and also by means of chemical reagents. If 10 parts of the linseed varnish under examination be stirred up with 3 parts of sulphuric acid in a suitable vessel and left to stand until the oil and acid layers have separated,

a white precipitate, containing the metallic compounds, is formed, whilst the varnish becomes dark brown, and the acid orange-yellow to yellow-brown, in colour when fish oil is present. On the other hand pure linseed oil varnish is at first greenish, turning later to brownish-green, whilst the acid assumes a more yellowish colour. When treated with chlorine gas, a linseed varnish adulterated with fish oil at once turns dark brown, and finally black; whereas, on the other hand, unadulterated varnish becomes more and more decolorised, owing to the bleaching action of chlorine on the vegetable fats and oils, the animal fats—with the exception of neat's-foot oil—on the contrary being always darkened in colour thereby and finally turned black. If 5 parts, by volume, of linseed varnish be boiled with 1 part of caustic soda lye (sp. gr 1.34) there results a yellowish emulsion in the case of unadulterated linseed varnish, or a red one when the varnish has been falsified with fish oil.

*Detection of Mineral Oils, Petroleum Derivatives.*

Mineral oils have a lower gravity than linseed oil, *i.e.*, 0.840 to 0.930.

Mineral oil, rosin oil, and unsaponifiable oils are generally detected and estimated by saponifying with caustic potash shaking out with ether, washing the latter, drying over calcium chloride and evaporating off the ether at a low temperature and weighing the residual oil.

*Adulteration with Rosin Oil.*

Rosin oil has a higher gravity than linseed oil, *i.e.*, 0.96 to 1.00.

Rosin oil is the most common adulterant of linseed varnish, and can in most cases be detected by the smell alone, this characteristic becoming more apparent if a few drops of the varnish under examination be rubbed between the hands until they become warm. The taste also affords an excellent

means for detecting the presence of even very small quantities of this oil, the irritant, nauseous flavour being recognisable directly. If varnish containing rosin oil be agitated with dilute sulphuric—or hydrochloric—acid and left to stand, there forms, in addition to the white precipitate of lead and manganese salts, a number of sticky, white lumps; whereas, with pure linseed varnish, only the first-named deposit is produced, and the liquid will have become thoroughly clarified after a few hours. Furthermore the (Fischer) oleometer can be employed for testing, pure manganese varnish registering  $26^{\circ}$  and lead varnish  $24^{\circ}$ , whereas varnish containing rosin oil will indicate barely  $20^{\circ}$  to  $22^{\circ}$ . A special peculiarity exhibited by all varnishes containing rosin oil is that when stored cold a part of the rosin oil is precipitated, the varnish becoming turbid, and a compact sediment is formed which disappears altogether when warmed. If a suspected sample of varnish be immersed in a freezing mixture at about  $5^{\circ}$  to  $6^{\circ}$ , the above phenomenon will make its appearance in a very short time when rosin oil is present; whereas pure linseed varnish remains pale and clear. The formation of a considerable quantity of sediment in linseed varnish during storage indicates, with certainty, adulteration with rosin oil. Again, 10 grams of the suspected varnish may be mixed with 50 c.c. of alcohol and 5 grams of caustic potash (dissolved in a minimum of water), and heated for half an hour under a reflux condenser, after which 50 c.c. of water are added and the whole is cooled by immersion in cold water. Then the liquid is shaken up with petroleum spirit in a separating funnel, and, after the two layers have separated, the lower stratum is drawn off as completely as possible. The stratum of petroleum spirit is next washed repeatedly with water, which is finally separated. As, however, a few drops of water will be drawn off along with the petroleum spirit, it is advisable to transfer the latter to a dry

flask, from whence it can be poured into the weighing flask. By this means the water remains adherent to the walls of the intermediate flask. The residual liquid from the first treatment with petroleum spirit is extracted to exhaustion with the same solvent and the total extract is united.

In order to afford a rapid test for the presence of rosin oil or mineral oils in the unsaponifiable matter obtained by the above method, it is shaken up with an equal volume of acetone. If the liquids are completely miscible, the liquid is rosin oil, or a mixture of the latter with a little mineral oil. A similar test may be performed with alcohol (sp. gr. 0.95) in which rosin oils sink, whilst mineral oils do not.

Another method for detecting adulterations with rosin oils, which it is said to reveal when present even in quantities too small to be discernible by the taste or smell, is described by Landolt as follows :—

About 5 to 10 c.c. of the oil under examination are placed in a test tube with 3 to 5 c.c. of pure concentrated commercial nitric acid and warmed on the boiling water-bath, a check experiment being made concurrently with a linseed oil of known purity, and the alterations noted.

Pure linseed oil will remain yellow, but oil containing rosin oil will turn red.

Rosin oil and rosin may also be detected by means of the Liebermann-Storch reaction. The oil to be tested is heated with acetic anhydride and cooled, the latter is then separated from the oil and one drop of concentrated sulphuric acid poured down the side of the tube. In presence of rosin or rosin oil a violet coloration is developed.

When prices of varnishes rule high, adulteration with turpentine oil, and even with benzol, is occasionally practised. If a few drops of such linseed varnish be rubbed between the hands, the odour of turpentine or benzol will become manifest; the falsification may, however, be detected with

greater certainty by a distillation test, whereby these volatile oils will be driven over, leaving the linseed varnish behind unaltered. By working with weighed quantities the percentage of adulteration can be determined from the amount of distillate collected.

*Detection of Driers in Linseed Varnish.*

It can be ascertained whether a given varnish has been prepared by the aid of lead or other chemical compounds, and the tests employed only lead to negative results—i.e., no precipitate is formed—in case air or oxygen gas has been used for oxidising the linseed oil. When the oil is boiled with metallic oxides or other chemical compounds capable of yielding up oxygen, metallic linolates are produced and remain in solution or chemical combination with the oil, from which they can be afterwards separated—by solution or precipitation—by the addition of dilute hydrochloric or sulphuric acid. This forms the basis of the method of detection. The varnish is mixed with about its own volume of sulphuric acid in a test glass, and watched for the formation of a precipitate. If a white deposit is produced, which turns black in presence of sulphuretted hydrogen, the varnish contains *lead*, and has therefore been boiled along with lead compounds, or, perhaps, been merely incorporated with such. If the acid remains clear and untroubled, but turns greenish, changing to black on the addition of sulphuretted hydrogen, then *copper* compounds have been employed. On the other hand, should the precipitate remain unchanged, lead is absent, and a further test is made, first with ammonia and then with ammonium sulphide. When *iron* is present a black precipitate is formed, whilst *manganese* gives a flesh-coloured, and *zinc* a white precipitate. Further indications are obtainable by treating the original acid solution with an aqueous solution of sodium

carbonate. A dirty-green precipitate implies *iron*, as does also the production of a blue coloration when potassium ferrocyanide is added to the solution. A white precipitate, turning blackish-brown on exposure to air, indicates *manganese*; and when *zinc* is present a white precipitate, soluble in excess, is formed on the addition of a little ammonia to the acid solution.

With regard to the manner in which varnish should be tested with reference to its suitability for use as paint, the following appropriate remarks were made by the late Professor Rudolf Benedikt:—

“Thanks particularly to Bauer and Hazura, and their pupils, our knowledge on the subject of linseed oil has been greatly increased during the past few years. We now know that the acid of linseed oil, so far from being a single substance, is a mixture of at least three acids, described by Hazura as linolic, linolenic, and iso-linolenic acid, and that a high proportion of the two latter is characteristic of this oil. The same workers have revised Mulder's labours, confirmed the majority of his results, and brought them into harmony with modern ideas of chemical composition. Moreover, the analytical examination of linseed oils and the fatty oils in general has developed to such an extent that we are enabled to identify and quantitatively determine with certainty—within definite limits—the presence of admixtures of rosin, rosin oil, and mineral oils. On the other hand, however, the detection of added fish oil or vegetable oils is, as yet, possible only in a qualitative sense, but not quantitatively. For the purposes of buying, the varnish maker has sufficient indications available to enable him to determine whether a proffered sample of oil is adulterated with rosin oil or mineral oils; moreover, he can determine the drying power by the Livache or similar method.

“When buying linseed oil the varnish maker will be sure

to choose the one exhibiting the highest iodine value, the greatest increase in weight under the Livache test, or highest thermal value (rise in temperature) when mixed with sulphuric acid. He should also fix a certain minimum for the iodine value, Livache value, and Maumené thermal value, notwithstanding that oils exhibiting lower values may be none the less pure. (The buyer might probably lay down these conditions. The seller, however, does not trouble himself about them if he sells 'pure linseed oil'.)

"It is, however, of importance that each of these methods of testing affords in itself an idea of the drying properties of the oil, and enables a comparison to be drawn as to the value of different oils. The determination of the specific gravity, viscosity, refraction, etc., may serve to supplement and confirm the results of analysis in dubious cases, but will seldom be necessary.

"A manufacturer should, for instance, make it a condition that the linseed oil supplied should have an iodine value of at least 170.

"In the case of linseed varnish, however, the conditions being different, it is impossible to demand that a good varnish must exhibit a given iodine value, a definite oxygen absorption value, or a particular degree of viscosity. Varnish has a lower iodine value, a higher acetyl value, greater specific gravity, and higher viscosity than raw linseed oil.

"During the boiling process the iodine value recedes, whilst the other specified values increase. Consequently, if one were to boil a pure linseed oil to varnish, and chemically examine the samples drawn from time to time, tabulating the results, a progressively decreasing series of iodine values and an inverse ratio of acetyl values would be obtained, though among the resulting products several might be good varnishes. The individual samples would differ among themselves in the rate of drying and degree of hardness attained.



but might all be useful varnishes. We have ourselves prepared almost equally good varnishes by boiling the same oil for different lengths of time with the same addition. The conditions are more complex when oils of different origin are boiled by different methods with different proportions of added materials.

"In judging the value of a varnish therefore from a chemical and physical examination it is only possible to come to a correct conclusion by taking into account the results of all the tests

"For instance, if one knows that a linseed varnish has an iodine value of 130, nothing is learned therefrom; it must first be ascertained what are the acetyl and Livache values and viscosity corresponding to a good varnish having the iodine value in question.

"However, sufficient experience has not yet been gained, with regard to the chemical and physical properties of good varnish, and many of the data published are too unreliable to suffice for the preparation of data. For this purpose it would therefore, in the first place, be essential to have at disposal a series of good varnishes, and to have these analysed by a competent chemist. Even then it is not certain that conclusive results would be obtained by this mode of procedure, since chemical practice shows numerous examples wherein analysis alone has led to no positive results.

"Meanwhile one cannot do better than test the drying power of a varnish by spreading out and exposure, which will also enable the consistency after drying, and the resistance to air, light, and water, to be ascertained. This plan is, however, beset with the disadvantage that defects only make their appearance after a comparatively long time; in this case, as in others, protection must be secured by obtaining the materials from firms known to be trustworthy. In addition to this a chemical examination, in certain directions,

*e.g.*, the admixture of rosin, rosin oil, mineral oils, fish oil, can be performed. Nevertheless, it should not be forgotten that a chemical examination sufficiently thorough to afford a comprehensive judgment of a linseed varnish—even premising that all the data for such judgment have been acquired—requires considerable time to carry out, and needs a highly skilled and expert chemist. It must not be imagined that such simple tests as are used for olive oil, *e.g.*, iodine value, and perhaps specific gravity determination will be sufficient.

“The considerable expense attaching to examinations of this kind, particularly when the comparison of varnishes offered by different sellers is in question, would be likely to preclude a systematic and general investigation.

“The examination becomes a still more complicated matter when ready-made paints are under consideration, because it then becomes necessary to separate the varnish from the mineral admixtures.”

The foregoing remarks are very instructive, showing, as they do, that it is possible to ascertain, both by analytical means and empirically, by a few simple tests, whether a linseed varnish is adulterated or not. They nevertheless throw no light on the question whether even a pure linseed varnish affords a guarantee of its suitability as an anti-corrosive paint. In the author's opinion this problem will never be solved, but that attention must be restricted to requiring—

1. That the linseed varnish contains no extraneous fatty oils, rosin, rosin oil, mineral oils, or any adjuncts whatsoever. (These are generally metallic rosin soaps dissolved in benzol or petroleum.)

2. That the varnish shall possess a certain consistency, to be determined by means of the viscosimeter.

3. That the varnish shall dry within twelve hours, and be set hard within a further twenty-four hours.

4. That it shall be pale in colour, perfectly clear, and deposit no sediment even after storage for a fortnight.

The paint manufacturer will buy the necessary raw material—linseed oil—in the chief commercial centres and work it up into varnish; he will know how to protect himself against adulteration, as well as to prepare his varnish so as to obtain a product that will comply with the conditions enumerated. In spite of all the progress that has been made, the purchase of the article is still a question of confidence, and an honourable manufacturer will not resort to adulteration in order to make a slight extra profit or a lower tender.

#### CHINESE WOOD OIL (WOOD OIL, VARNISH TREE OIL, OR TUNG OIL).

Even in older chemico-technical works brief notices are to be met with on the wood oil of China and Japan, which is obtained from the seeds of the varnish tree (*Aleurites cordata*, *Elaeococca vernicia*) in those countries, and is sold there as a varnish oil for waterproofing wood, caulking ships, and lacquering furniture. About 200,000 Chinese piculs (1 picul = 133·33 lb., or 60½ kilos.) are annually dispatched from Hankow on the Yang-tse-Kiang to other parts of China.

According to de Negri and Sburlati, the fruit of the varnish tree contains 53·25 per cent. of oil, about 42 per cent. being obtainable by pressing, etc. The same authorities also state that the oil is clear, of a yellowish colour, and having a peculiar smell resembling that of castor oil. It is tasteless, dries in about twenty-four hours when exposed to the air, and is soluble in cold, absolute alcohol. By solution in carbon disulphide, and evaporation of the solvent, the oil is converted into a crystalline mass. According to another report the cold pressed oil is pale yellow, whilst that obtained by warm pressing is almost dark brown. It is a thick oil of high density (0·9406–0·9440), and does not solidify in the cold. This oil, which possesses much stronger drying properties than candle-nut oil from *Aleurites triloba*, must not be confounded with

the balsam known as wood oil, or Gurjun balsam, derived from *Dipterocarpus turbinatus* Gaertn.; the latter is, however, adulterated with wood oil. The examination of the oil by Cloez showed it to consist of two glycerides, ordinary olein and another glyceride—elæomargarin—the latter yielding, on saponification, elæomargaric or margarolic acid  $C_{18}H_{30}O_2$ . This report has, on account of the formula, but little pretention to accuracy. The formula of elæomargaric acid is  $C_{18}H_{32}O_2$ . In drying power it is superior to linseed oil, but the warm-pressed oil appears to be endowed with this property in a less degree than that from cold pressing.

When heated with alcoholic potash it saponifies rapidly.

### *Constants of Wood Oil.*

Many analyses of Chinese wood oil have been made, but it is questionable as to how far these relate to pure samples. The following are analyses of seventeen samples of Hankow oil by A. Chaston Chapman (*Analyst*, Dec., 1912).

Sample No.	Iodine Value	Specific Gravity at 15 5° C.	Saponification Value.	Refractive Index at 20° C.	Time of Efflux, Seconds.	Heat Polymerisation Test, 1 Hour at 250° C.
1	169.9	0.9419	196.6	1.5207	2178	Very hard
2	168.4	0.9406	198.8	1.5181	1636	Hard
3	166.5	0.9426	194.8	1.5190	1946	Fairly hard
4	166.4	0.9417	198.0	1.5170	1880	"
5	168.8	0.9430	195.6	1.5195	2017	Very hard
6	170.0	0.9440	194.5	1.5180	1849	Hard
7	168.6	0.9416	193.0	1.5150	—	Fairly hard
8	171.0	0.9414	192.0	1.5170	—	Hard
9	169.7	0.9437	194.1	1.5176	1997	"
10	173.0	0.9430	192.5	1.5165	1722	"
11	176.2	0.9417	192.0	1.5168	1605	"
12	172.6	0.9429	196.0	1.5180	1740	"
13	174.2	0.9427	194.6	1.5182	1690	"
14	173.7	0.9430	195.0	1.5194	1820	"
15	172.8	0.9440	194.6	1.5193	2047	"
16	169.5	0.9420	195.2	1.5160	1804	"
17	169.6	0.9433	195.2	1.5187	1820	Very hard
Average	170.6	0.9425	194.2	1.5179	1850	—

Lewkowitsch (*Oils, Fats, and Waxes*, 5th ed., Vol. II., p. 75) gives the following constants for Chinese wood oil :—

Specific gravity at 15.5° C. . . . .	0.938 to 0.9440
Solidifying-point . . . . .	2 „ 8° C.
Saponification value . . . . .	185.1 „ 197
Iodine value . . . . .	150.2 „ 176.2
Refractive index at 20° C. . . . .	1.511 „ 1.5207
Insoluble fatty acids . . . . .	95.0 per cent.
Solidifying-point . . . . .	81°-2 C.
Melting-point . . . . .	40° to 48.8° C.
Neutralisation value . . . . .	188.8
Iodine value . . . . .	145.0 to 159.4

According to Chapman the refractive index is the highest of all oils, rarely falling below 1.517. The viscosity is also much higher than that of any oils with which it is likely to be adulterated.

A very characteristic test for the purity of Chinese wood oil is the heat polymerisation test (Bacon's or Worrall's test). If the oil be rapidly heated in a basin on a sand-bath to a temperature of 280° C. and stirred it will become a perfectly solid dry jelly in ten minutes if pure, but if adulterated it will be soft, or more or less fluid.

If 5 grams of the oil be mixed with 2 c.c. of carbon bisulphide and 2 c.c. of sulphur chloride, and stirred in the cold, a thick, sticky jelly is formed. At the boiling temperature of water a skin begins to form on the surface of the oil within one quarter of an hour, and entirely covers it in two hours. At the end of four hours' heating the increase in weight amounts to 1.14 per cent.

The elaidin test gives a dark brown-red mass, consisting of a heavy, almost solid portion and an oily residue, the whole being thick when stirred up. With Becchi's reagent a deep brown-red coloration is produced. Strong sulphuric acid converts the oil into a solid black mass, and nitric acid (sp. gr. 1.4) forms with the oil a viscid mass, which deepens in colour and becomes brittle on standing. If 9 grams of oil

be dissolved in 5 c.c. of chloroform, and stirred up with 5 c.c. of a saturated solution of iodine in chloroform, the mixture sets to a stiff jelly in two minutes; when only 2 grams of oil are taken the mass is so hard that it can be granulated. On exposure to a heat of  $180^{\circ}\text{C}$  with exclusion of air, a small volume of vapour is evolved without the fluidity of the oil being diminished; but above  $250^{\circ}\text{C}$ . the oil is changed into a solid, clear elastic substance which is insoluble in the ordinary solvents for oils, and does not melt at the temperature of its formation.

According to the statements of importers, there are two kinds of wood oil: Canton wood oil and Hankow wood oil, the former being purer, better, and about 10 per cent. higher in price than the Hankow oil.

The author's experience of this oil goes to show that it is of a pale yellow colour, clear—or at most only slightly turbid, and then clarifying within a few days—and much thicker than linseed oil, in fact about the same as castor oil. The odour is peculiar but not unpleasant, approximating most nearly to earth-nut oil, the same applies also to the taste. When heated to  $200^{\circ}\text{C}$ . it soon undergoes considerable alteration, and also rapidly thickens with litharge, the colour then becoming darker. A faint odour of acrolein is evolved during heating. At  $260^{\circ}$  to  $280^{\circ}\text{C}$ . the oil merely gelatinises, but at higher temperatures it is changed to a solid gelatinous mass, the vapours igniting spontaneously. When manganous borate is used as the drier, the initially thin liquid changes suddenly into the gelatinous condition, and is then no longer soluble in benzol or turpentine oil, therefore care is required to prevent the occurrence of this modification.

With regard to the drying properties of the oil, the following points may be mentioned: when spread out in a thin layer on glass it dries, in a closed room, within twenty-

four hours, or so, to a whitish film, so that the glass is no longer transparent but resembles milky or frosted glass. If the layer is thick, a longer time is occupied in drying. On exposure to the air, however, even the thicker layers dry within a few hours. The oil, after being boiled or heated by itself, also develops the aforesaid whitish film; but, after boiling with litharge, dries as clear and bright as any other oil varnish. Its greatest peculiarity is exhibited after drying, since whereas linseed oil, linseed varnish, and all other drying oils form a thin superficial skin which gradually becomes thicker and thicker, drying from above downwards, wood oil dries uniformly throughout, so that the lower portion is just as dry as the surface. Even fairly thick layers can be scraped off as a tough or somewhat brittle mass, quite uniform throughout. One point worthy of note is the exceptionally slight degree of adhesion of the dry coating to glass surfaces.

Although the price of wood oil is still so high that it cannot be regarded as a competitor of linseed oil, it has nevertheless made its way in the varnish and paint-making industries, by reason of its special rapid-drying properties; there is no doubt that when it has been thoroughly experimented with, it will find application in a number of ways. For example Chinese wood oil is, on account of its hardness, used as a floor varnish; and in the waterproofing industry it has been worked up into a product ("Atcella") resembling oilcloth, which is superior to the latter by reason of its unusual elasticity. Whether the oil will be found suitable for use on ironwork, particularly for the primary transparent coating, remains to be proved.

In the raw state, however, wood oil cannot be used, because it dries somewhat opaque. In order to be able to use it in the same way as linseed oil it must be heated, and that too with a small percentage of lead oxides (red lead or

litharge), since otherwise it will still dry opaque. This, of course, makes no difference when it is used in paints, but even then the treatment is desirable in order to accelerate drying. In heating the oil, whether with lead compounds or those of manganese, the temperature must be carefully kept below  $200^{\circ}\text{C}.$ ; otherwise, and particularly in the case of manganese compounds (*e.g.*, manganous borate), thickening ensues quickly developing into complete gelatinisation, which spoils the product for use. Consequently the temperature should not exceed  $160^{\circ}\text{C}.$ , or  $180^{\circ}\text{C}.$ , as a maximum; and when this is reached the pot should be removed from the fire—or the latter extinguished—before the driers are stirred in. This will be quite sufficient to impart the requisite drying power to the oil, and will at the same time obviate the evil already referred to. When ground with pigments, the oil prepared in this manner furnishes excellent paints, which dry right through in a short time, and set hard and solid, unlike linseed oil paints, which harden on the surface but remain soft and tacky underneath for a long time. There is a good demand for paints that will dry thoroughly, and for these the question of price is a minor consideration.

Its predominating quality renders wood oil also suitable for the manufacture of oil lacquer varnishes. Nevertheless, both in its employment for this purpose and as a vehicle for paints, the chief thing to be borne in mind is the above mentioned tendency of the oil to gelatinise at temperatures approaching  $200^{\circ}\text{C}.$ , when containing additions of lead or manganese compounds. Very good results are obtainable by the association of wood oil with linseed oil.

The odour of Chinese wood oil is very peculiar and clings persistently to the varnish prepared from this oil, even long after the coating of varnish is dry; in fact it is so persistent that the smell is still decidedly apparent after waterproof articles prepared from this oil and dried by hot air have been



stored for months, just as oilcloth smells of linseed oil for years. Of course this peculiar lard-like smell is also noticeable in the varnishes made from wood oil, and if objected to it will evidently be necessary to remove it, as far as possible, or at least to reduce it to a minimum. Masking the smell by the use of ethereal oils is not likely to accomplish the desired effect, since as the former are dissipated the odour of the oil will reappear. Consequently other means must be adopted, such, for example, as agitation with a dilute solution of permanganate of potash, a filtered solution of chloride of lime (bleaching powder), filtration through animal charcoal, or stirring up with flour or potato starch and leaving a long time to settle, followed by filtration. It is claimed for the process introduced by Bang and Ruffin that almost perfect deodorisation may be effected by means of dried atmospheric air. To this end the oil is warmed in a suitable pan and subjected to a current of air (blown through it by a fan) at a temperature not exceeding  $50^{\circ}$  C for at least six or eight hours, at the end of which time the smell of the oil will have diminished considerably, so that it becomes unobjectionable.

Mention must not be omitted that wood oil should not be regarded as a substitute for linseed oil. On the contrary, it yields varnishes, paints, and lacquers endowed with special properties; consequently no great stress need be laid on the necessity for deodorisation, since the peculiar smell of the oil may serve as a characteristic of these new products, and all the more so as it is not disagreeable.

## CHAPTER V.

### PIGMENTS

THE second constituent of all paints is the pigment, by means of which covering power and suitable consistency are secured, pure linseed varnish forming only a transparent coating of a very attenuated nature. In order to impart the proper thickness to the paint and render it non-transparent the linseed varnish is mixed with a powdered pigment and ground along with the same in a colour mill, so that the requisite fineness and intimate admixture may be obtained. Every paint is a mixture of linseed varnish and pigment, and the latter can be recovered by leaving the mass to settle and then washing with benzol or ether; so that the pigment can be extracted from any oil paint and tested as to its composition. When a paint containing a lead product as pigment is kept for a long time, the latter may, under certain circumstances, exert chemical influence on the linseed varnish; whereas pigments free from lead are inert in this respect. This is an important point, and one that must be borne in mind continually, in order to prevent the formation of false conclusions. Whilst many pigments are incapable of acting on linseed varnish, it may happen that, through the presence of extraneous substances in the pigment, or as a result of the method of preparation, or from other causes, some action is initiated. Thus, in the case of iron oxide pigments prepared from the residues from alum works, it may easily happen that an acid reaction is exhibited, which may have an unfavourable effect on the varnish. Moreover, water exerts a peculiar effect on these

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paints. If a paint containing ochre or red oxide be covered over with water and left for some time, it will be found that instead of forming a homogeneous mass the paint will become granular, a portion of the oil being displaced by water. This may be due to the greater affinity of the pigment for water than for oil or to the formation of an emulsion.

As already stated, the pigment plays the second leading part in all paints. The linseed varnish imparts elasticity, cohesion, and capacity of resisting external influences, whilst the pigment gives covering power and colour. Sufficient attention having already been given to the varnish, we will now turn to the pigments.

All pigments employed for paints to be used on iron-work are of inorganic nature, some being found native and others produced by chemical means. Accordingly a distinction may be drawn between—

1. Natural earthy pigments and
2. Chemically prepared pigments.

Both these classes are used in paints for iron. To the former category belong all pigments containing iron oxides in larger or smaller proportions, such as ochre, colcothar, Venetian red, iron minium, and the scaly oxides of iron; in addition to which there are others, not finding employment for this purpose, such as Terra di Siena and manganese pigments, like umber. Graphite, which consists of more or less pure carbon, also belongs to this class.

The class of chemical pigments comprises a large number of pigmentary bodies, mostly compounds of the heavy metals, lead, antimony, zinc, iron, copper, chromium, etc., prepared by oxidation, treatment with acids, or by precipitation from various saline solutions. It is not necessary to enumerate all the known pigments, seeing that most of these are of no value for our immediate purpose, therefore the author will restrict himself to the consideration of such as are employed

almost exclusively in the preparation of anti-corrosive paints. These are: the pigmentary compounds of lead, zinc, and iron, as well as graphite. The other pigments used, such as vine-black, ultra-marine, etc., are only employed in small quantities for toning purposes and have no influence on the quality of the anti-corrosive paints. Consequently the pigments with which we are concerned can be divided into three principal groups, namely:—

1. Lead pigments,
2. Zinc pigments,
3. Iron pigments,

a fourth group consisting solely of graphite. The chief representatives of the three groups in question being:—

*Lead group*: Red lead (minium), white lead.

*Zinc group*: Zinc white, zinc grey, lithopone (permanent white, zinc sulphide white), calamine white, milled zinc ore, zinc silicate.

*Iron group*: Native oxides of iron, such as colcothar, burnt ochre, iron minium, scaly iron oxides, artificial iron oxides, *Caput mortuum*—this latter body being frequently sold as colcothar.

The *Carbon group* is represented by graphite as the principal constituent of a pigment, with vegetable charcoal or lamp black as auxiliary.

Before proceeding to the further consideration of the suitability of the various pigments for anti-corrosive paints it will be necessary to briefly describe the pigments themselves.

### 1. *Lead Pigments.*

(a) *White lead*—The basic carbonate of lead or white lead—usually called “lead oxide” in Germany and Switzerland—has approximately the formula  $2(\text{PbCO}_3) \cdot \text{PbH}_2\text{O}_2$ . It is prepared from metallic lead in three different ways: by the Dutch method; the chamber or Austrian method; and by

the wet or French method, wherein the carbonate is precipitated by carbon dioxide from a solution of lead acetate. Latterly, attempts have also been made to prepare it by electrolytic means. The covering power of the product so obtained by these methods varies, owing to differences in structure.

Good white lead is pure white, heavy, and readily pulverulent; insoluble in water, but soluble in caustic potash or caustic soda, and also dissolving, with effervescence, in nitric acid or acetic acid. In boiling hydrochloric acid it dissolves, but, on cooling, the solution deposits fine needles of lead chloride, soluble in boiling water. Solutions of white lead in acetic acid yield a black precipitate of lead sulphide with sulphuretted hydrogen or ammonium sulphide, and a white precipitate of lead sulphate with sulphuric acid. Neutral solutions give with potassium bi-chromate a yellow precipitate of lead chromate (chrome yellow). When heated to  $400^{\circ}$  C. the carbonate parts with its carbon dioxide and water, lead oxide being left as a residue.

The quality and appearance of the product vary according to the method of preparation employed, the Dutch process yielding a very heavy grade of inferior colour but considerable covering power, whilst the French process (precipitation method) gives a very white product of inferior covering power.

The difference in covering power of the various grades of white lead is due to differences in the size of the aggregates. The precipitated white lead of low covering power is loose, coarse grained, and not infrequently crystalline. That obtained by the Dutch method is denser and fine grained; whilst the French article is crystalline in structure. In point of covering power, therefore, white lead is inferior in proportion as its crystalline character is more decided, which will be the case when the proportion of lead carbon-

ate has been considerably increased during the process of manufacture, this compound being capable—apart from its great hardness—of rendering the white lead unfit for use. An excess of lead carbonate also tends to produce greyness.

The principal adulterant of white lead is Barytes (natural or artificial barium sulphate—permanent white). Pure white lead should dissolve completely in dilute nitric acid (1 : 2 water). The nitric acid must, however, be chemically pure, and free from hydrochloric or sulphuric acid, since the former would produce the almost insoluble chloride, and the latter the insoluble sulphate; it must also be dilute.

On the addition of sulphuric acid the insoluble lead sulphate is thrown down; after removing this by filtration the filtrate should afford no precipitate, or even turbidity with ammonia, ammonium sulphide, or ammonium oxalate. A white precipitate occurring on the addition of ammonium sulphide indicates the presence of zinc white, whereas a white precipitate produced by ammonium oxalate reveals added chalk. If the white lead did not entirely dissolve in dilute nitric acid, the insoluble matter probably consists of barium sulphate, in which lead sulphate, China clay (kaolin), gypsum, strontium carbonate and strontium sulphate scarcely ever occur as adjuncts. The residue on the filter is boiled with strong hydrochloric acid and set aside to cool, the precipitated lead chloride being then filtered off and the filtrate tested with barium chloride, a white precipitate is formed if lead sulphate be present. Another part of the filtrate is diluted and treated with gaseous sulphuretted hydrogen, which throws down the lead sulphate in the form of sulphide. This being filtered off, the filtrate is boiled to expel the sulphuretted hydrogen, and, after re-filtering, treated with strong ammonia. A white precipitate of alumina indicates China clay. This is separated by filtration and the liquid is tested with ammonium carbonate, which in presence of

gypsum or chalk forms a white precipitate. A small portion of the residue insoluble in hydrochloric acid is taken up by a platinum loop and held in a Bunsen flame; a green coloration indicates barium, and a red one strontium.

(b) *Red lead* (minium; lead tetroxide).—The true fundamental constituent of red lead is the tetroxide  $Pb_3O_4$ , but the commercial product contains, in addition, more or less lead monoxide (litharge). It is prepared by roasting metallic lead into the monoxide litharge, and converting the product into minium in calcining ovens. Red lead intended for paints must be free from metallic lead, since the presence in the latter of impurities, such as antimony, copper, iron, etc., would spoil the colour of the paint when dried.

Minium is a heavy, red powder, approximating in shade to orange, and having a specific gravity of 8.3. It darkens when heated, but resumes its original colour on cooling. Acids attack it to a greater or smaller extent, but when in use as a paint it is very fast to light and the effects of the weather; neither is it attacked by moisture. It cannot, however, be used where sulphuretted hydrogen gas is evolved, since this gas turns the colour brown to black, in consequence of the formation of the sulphide. Red lead is seldom adulterated, the only substance used for this purpose being red iron oxide.

Pure, concentrated nitric acid decomposes red lead, and should form a colourless solution when water is added. A yellow coloration indicates iron, which may be confirmed by the formation of a blue precipitate with potassium ferrocyanide after dilution.

Insoluble matter, such as brick dust and the like, is left as a residue and may be examined further. An addition of barytes reduces the colour of red lead.

To determine its purity, 2 grams of the red lead to be tested are dissolved in concentrated nitric acid, and, after

diluting and filtering, the whole of the lead is thrown down by sulphuric acid in presence of a little alcohol. The precipitate is washed with water on the filter, and, when dried, is calcined in a crucible, being thereafter cooled in a desiccator and weighed. The resulting weight, multiplied by 0.955, gives the amount of *pure* red lead. The liquid filtered from the lead sulphate precipitate may be tested for iron.

Red lead can be detected in mixed paints by the dark brown coloration it gives with dilute nitric or acetic acids, and by answering to the characteristic tests for this metal—white precipitate with sulphuric acid and a yellow one with potassium iodide.

In a pamphlet by G. W. Thompson, issued by the National Lead Company of the United States, it is stated that true red lead should contain approximately 100 per cent. of  $\text{Pb}_3\text{O}_4$  and little or no litharge, commercial red leads, however, contain anything from 70 to 95 per cent., or even a little higher, the remainder being litharge. The presence of litharge in red lead must not be regarded as adulteration but rather as evidence of faulty manufacture. He states that highly oxidised red lead is finer than that containing litharge, keeps its colour better, and is a better preservative against atmospheric influences; besides a paint made from it will spread further and still give excellent results although the coating is thinner than could be obtained with a paint containing the more gritty litharge. In the tests carried out on the Havre de Grace Bridge by the American Society for Testing Materials, the three best results were obtained with paints consisting entirely or almost entirely of red lead, those coming nearest to them containing some red lead, while those which had least preservative action contained no red lead. The best result of all was obtained with a paint the pigment in which contained 95.9 per cent. of red lead, in the second the pigment contained 88.5 per cent. of red lead, whilst in the third best the pigment consisted mostly of red lead.



Mr. H. Gardner, Director of the Scientific Section of the Educational Bureau of the Paint Manufacturers' Association, in a Bulletin (No. 52) on Marine Paints states, however, that in priming paints for ships the red lead should not be pure, but should contain a percentage of litharge (10 to 15 per cent.), which combines with the oil to form a cement-like compound of linoleate. This is also the view put forward by Dr. John A. Schaeffer in a paper read before the Pennsylvania State Convention of Master House Painters and Decorators in 1917, in which he criticises the results obtained in the Havre de Grace Bridge tests, showing that the proportions of oil and pigment in the two red lead paints varied very materially, and that when these were kept constant the best results were obtained with the lower percentages of red lead. In a series of tests carried out at the Institute of Industrial Research, Washington, in 1911, all variables were as far as possible eliminated, with the exception of the true red lead content as far as this was compatible with the physical structure of the pigment employed. The paints tested were as follows:—

Panel No.	Pigment.	$Pb_3O_4$ Content.	Pigment in Paint.	Linseed Oil in Paint	Weight per Gallon in lb.
1	Red lead	86 per cent.	80	20	27
2	"	88 "	80	20	25
3	"	90 "	79	21	28
4	"	93 "	78	22	24
5	"	95 "	80	20	27
6	"	99 "	72	28	21
7	Red lead in paste form	99 "	—	—	—

After two years' exposure an examination showed that Nos. 1, 2, and 3 were in the best condition, corrosion being absent and the original red colour of the paint retained. Nos. 4, 5, 6, and 7 are lighter in colour due to disintegration of the surface film and formation of lead carbonate due to the action of the carbonic acid in the atmosphere

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It is interesting to know that the specifications for the U.S. Navy are now altered, the requirements being for red lead that it should contain 82 to 88 per cent. of  $Pb_3O_4$  instead of 94 to 97, which up to recently had been the percentages fixed. The Public Service Corporation specify 85 to 90 per cent. of  $Pb_3O_4$  in their contracts.

It is, however, clearly stated by the above author that the litharge present in  $Pb_3O_4$  should be there *per se* and not as an added constituent, as in the latter case it would be found to lead to serious trouble. Dr. John A. Schaeffer, in his paper read before the Pennsylvania State Convention of Master House Painters and Decorators, refers to sublimed blue lead as an excellent pigment for use in paints for protective purposes, instancing in its favour, high basicity, exceptional durability, extreme fineness and smoothness, easy brushing and spreading, remarkable opacity, and elasticity and toughness in oil.

## 2. Zinc Pigments.

(a) *Zinc white*, zinc oxide, is non-poisonous and is unacted on by sulphuretted hydrogen. It is prepared by heating metallic zinc to pale red heat in retorts, whereupon the metal volatilises and the vapours ignite, forming zinc oxide. It may also be prepared by the wet method, by decomposing a salt of zinc. The product obtained from zinc ores is seldom pure, but mostly contains variable quantities of cadmium, which considerably modifies the purity of the colour.

Zinc white is a white, loose powder, devoid of smell or taste, and with a decidedly bluish tinge. It dissolves to a clear solution in acids, strong ammonia, and alkalis, and resists the influence of atmospheric air and light, as well as sulphuretted hydrogen and sulphurous gases, with which it forms white, colourless compounds. It is therefore highly suitable for use as a pigment.

The commercial article should contain not more than 2

per cent. of moisture. This can be determined by drying a weighed quantity at  $100^{\circ}$  C. Barytes and China clay are the adulterants employed, and the water content is often artificially increased—in order to cheapen the product—to as much as 10 per cent. by damping it with glycerine.

Zinc white ought to dissolve to a clear solution in nitric acid, with only a trace of effervescence; a residue will indicate the presence of barytes or China clay. The first-named can be detected by its high specific gravity, but gives no coloration to the Bunsen flame; whereas China clay imparts a yellowish-green tinge to the flame. On boiling the residue with concentrated sulphuric acid for some time barytes remains undissolved, while China clay passes into solution. On diluting the filtrate, after cooling, and then adding ammonia, a white precipitate of alumina indicates China clay, barytes giving no precipitate. Effervescence during solution indicates that the zinc white probably contains lead carbonate or zinc carbonate; in the latter case the solution will turn brown to black on the addition of sulphuretted hydrogen, or a similarly coloured precipitate will be formed. On neutralising the nitric solution with ammonia the whole of the zinc can be thrown down by ammonium sulphide (the precipitate must be white, otherwise the presence of extraneous metals is indicated). The resulting filtrate should give no precipitate with ammonium oxalate, otherwise gypsum or whiting will be indicated.

(b) *Zinc grey* is a by-product of the manufacture of zinc white, being zinc oxide contaminated with metallic zinc and carbon, which latter substance it leaves behind as a residue when dissolved in hydrochloric, nitric, or sulphuric acid. The solution gives a white precipitate with potassium sulphide or ammonium sulphide, after neutralisation with ammonia or an alkali carbonate. Zinc blende (ground) is often met with in commerce as zinc grey.

(c) *Lithopone*, permanent white, patent zinc white, sulphopone, enamel white, zinc-sulphide white, Charlton white, Griffith's patent zinc white, principally consists of zinc-sulphide, with an admixture of "blanc fixe" (barium sulphate). It is prepared by the wet method by mixing zinc sulphate, ammonium sulphide, and barium chloride, all in a state of solution. Lithopone varies according to the method employed in its production, and does not form any uniform chemical compound. It is imperfectly soluble in acids, and when treated with hydrochloric acid the clear portion of the solution gives the reactions for zinc, in addition to which calcium and magnesium can also be detected therein if present. Barium is present in the residue. Used alone zinc sulphide possesses good body, but is not quite pure white in colour, to remedy which defect it is mixed with other white pigments.

### 3. *Iron Pigments.*

The basis of all iron pigments is iron oxide. In the condition of hydrate it forms the colouring matter of ochre, sienna, umber, etc., all highly appreciated pigments, not merely on account of their durability and permanence in air and light, but also by reason of the extremely wide range of shades they produce. Iron oxide is frequently found native in large quantities in the form of hematite, limonite, etc., though never in a perfectly pure condition. Of the three chemically different oxides of iron, the peroxide  $\text{Fe}_2\text{O}_3$  (ferric oxide) is the most plentiful in nature and the purest form of the ore, and is used for the production of metallic iron. In the amorphous state it is for the most part accompanied by clay and the like, on which account the mixtures appear suitable as pigments and are frequently used as such. The colour of these natural mixtures ranges between dark red and black. When in the condition of hydrate, as limonite or yellow ochre, the colour is brownish to yellow-brown.

The pure peroxide of iron is readily soluble in acids, especially in concentrated nitric acid, or a mixture of nitric and hydrochloric acids (*aqua regia*), but less easily so in sulphuric acid or dilute nitric acid, compounds of iron being formed.

The various natural peroxides of iron differ in their degree of solubility, some dissolving very readily, others are extremely difficult to bring into solution, while others again are quite insoluble. It is only after exposure to the air for some time that any change occurs in the solution. If a solution of a ferric salt is treated with caustic potash, strong ammonia, or caustic soda solution, ferric hydrate is thrown down in the form of a brownish-red precipitate  $\text{Fe}_2(\text{HO})_6$ , which loses its water of hydration on heating and is converted into red ferric oxide,  $\text{Fe}_2\text{O}_3$ . Ferro-ferric oxide,  $\text{Fe}_3\text{O}_4$ , occurs in large quantities in nature as magnetic iron ore or magnetite, and is used in making iron. It is very difficult to dissolve in acids, the solutions containing ferrous and ferric salts.

The pigments known as the iron colours are, as already stated, prepared either from the native oxides, or by chemical means, and of course differ in composition; that is to say, they are all iron oxides containing varying proportions of other substances which exert considerable influence on their applicability.

#### (a) Natural Iron Pigments.

(i.) *Iron Minium*.—This is a dark-red to red-brown product, of metallic lustre, consisting of a mixture of hæmatite and varying proportions of alumina, the percentage of iron oxide attaining as much as 88 per cent, and even 90 per cent. For the production of iron minium the iron ore, in a roasted or unroasted state, is broken down and levigated, the washed mass being then air-dried, calcined in iron drums, ground to fine powder, and sifted. Usually pure, highly ferruginous

lumps are picked out and thoroughly roasted in a furnace, to drive out the water of hydration, the ore then forming a reddish-blue mass when cold. So prepared, the ore is taken to the stamping mill, the trough of which contains water to a depth of some thirty inches. A continuous supply of water is provided, the overflow running off through the overflow pipe in a reddish stream, discharging into a channel about twenty-five feet long, which conducts the water, with its content of suspended particles of iron oxide, into large settling tanks, where the water soon clarifies and whence it runs away clear. The heaviest particles of the crushed ore and the coarser granules are deposited in the channel, and these, after being ground in a roller mill, are mixed with water and conducted to the settling tanks; the resulting coarse deposit consists for the most part of fine quartz granules, which is removed. The very fine mass in the tanks is dried so as to contain not more than 3 to 4 per cent. of water, the resulting lumps being ground fine, sifted, and converted into dust. The product is a dark-red impalpable powder, consisting of iron oxide with more or less clay up to as much as 25 per cent.

(ii.) *Iron Oxides of Scaly Appearance.*—These are of a special character, resembling mica in appearance, being obtained from iron ores, such as red ironstone, hematite, and specular iron ore. For some years past they have been employed in the preparation of anti-corrosive paints.

Red ironstone, hematite, and specular iron ore, which all consist of iron oxide, occur more frequently and in more varied forms than the magnetic ore. They are found in the crystalline state (iron-glance) as hexagonal rhomboidal crystals, the ground plan of which is a hexahedral rhomboid, with terminal angles of  $96^\circ$ . It also forms tabular crystals with alternating inclined lateral facets, whilst in other cases the edges are sharp owing to the conjunction of the basal



surface with a hexagonal pyramid, which on the other hand is combined with the fundamental form, the basal surface, and other forms. The simplest plates, such as those which form, by association, the so-called "iron roses" found at St. Gothard, have perpendicular lateral facets through a hexagonal prism. The forms assumed by the combinations are highly diversified, the crystals being mostly fully developed, and single or in groups. Frequently they occur as dense masses, with a foliaceous to scaly, granular, and columnar to fibrous structure, the granular form in particular passing over into a dense mass through progressive decrease in the size of the individual crystals. The lamellar aggregations also form shaly masses, iron-glance shale, whilst the lamellar crystals are also termed iron-glance or micaceous iron on account of their resemblance to mica. Hæmatite occurs in this form ingrown in various kinds of rock, whilst very fine scales are found as an incrustation, and are termed "iron roses". The fibrous form occurs as globular concretions (bloodstone or kidney iron ore), and finally there is the earthy form (red ochre or ruddle), in which case the hæmatite is usually impure, containing an admixture of clay.

Decidedly crystalline in form, hæmatite exhibits imperfect cleavage parallel to the fundamental structure and the basal surfaces; is iron-black to dark steel-grey in colour, with a metallic lustre, opaque, and with a dark-red streak: as such it is termed iron-glance or specular ore. The lamellar form has the same appearance, but its very thin lamellæ are a transparent blood-red and also red externally. In the granular crystalline to dense forms the colour is reddish-grey to blood-red, as is also the case with the fibrous form, the streak being blood-red, but the lustre only semi-metallic. The earthy form is blood-red and dull.

Hardness = 5.5°; specific gravity = 5 to 5.2.

The composition is represented by the symbol  $\text{Fe}_2\text{O}_3$  with

70 per cent. of iron and 30 per cent. of oxygen. Occasionally a little titanous acid is present, which, combined with iron oxide, as  $\text{FeO}$ ,  $\text{TiO}_2$ , replaces small quantities of the oxide, as in the so-called "iron roses," on which account these latter are distinguished from hæmatites and termed "vasomelan," their streak being only reddish-black to black. It is infusible before the blowpipe, and becomes magnetic in the reducing flame. When heated with borax and phosphates it behaves like magnetite, giving a strong iron reaction; in the form of powder it will dissolve in acids, especially after prolonged boiling.

Hæmatite is of very frequent occurrence, the dense masses forming one of the best ores of iron, being always utilised for the production of the metal, by smelting, wherever met with in sufficient quantity.

To the hæmatite group belongs also the octahedral martite found in Brazilian micaceous iron shales, and forming a pseudometamorphic magnetite. This, though black in colour, leaves a red streak.

With regard to the differences between the materials yielded by iron-glance and micaceous iron ore, the following particulars may be given:—

When individual scales of the two ores are examined under a microscope (100 diameters) they will be found to exhibit by transmitted light the fine reddish colour proper to hæmatite, whilst by reflected light the iron-glance is more of a steely-grey, the coarser particles preventing the transmission of light under these conditions.

The colour of the scaly forms of iron oxide is various, ranging from silver-grey to iron-grey, sometimes reddish, in which case the colour of the powdered substance is more of a violet-brown red. They consist of silica, alumina, iron oxide, traces of phosphoric acid, manganese protoxide, lime, magnesia, alkalis, and water.

(iii.) *Spathic Iron Ore* (*sphaerosiderite*, or *white iron ore*).

—The finely ground mineral is met with in commerce as a pigment for anti-corrosive paints, under the name of *montanite*.

(b) *Artificially prepared Oxides of Iron.*

These pass under various names—such as *Caput mortuum*, English red, Prussian red, brown-red, Prague red, colcothar, jeweller's rouge, etc.—and are prepared either by the wet or the dry method. In the former, iron pyrites is roasted and then kept in a moistened condition for a long time, ferrous sulphate being formed by oxidation; the residual iron oxide is then merely subjected to calcination. A good deal of *Caput mortuum* is produced by calcining alum refuse, or vitriol refuse. In the wet process the iron oxide obtained by precipitation from solution is mostly converted into the red modification by calcining the precipitate.

Usually neither the native nor the artificial iron oxides are chemically pure compounds, but contain, in addition to the main constituent, such other bodies as clay, silica, gypsum, etc. Moreover, the pure iron oxide is not what is required as pigment, the presence of one or more foreign substances being frequently essential to the production of the desired shade of colour.

The percentage of moisture in iron oxide pigments is determined by drying a weighed quantity of the pigment at 120° C. in a drying oven until constant. The water of combination is then estimated by heating the dried substance to redness for an hour in a tared porcelain crucible, and weighing after cooling in a desiccator. The united results give the total amount of water present. To ascertain the other constituents of the substance 5 grains are treated with *aqua regia* until fully dissolved, the whole being then evaporated to dryness, treated with dilute hydrochloric acid, and filtered

into a half-litre flask, the residue on the filter washed with water, and the contents of the flask made up to the mark. The filtrate is employed for further investigation, whilst the insoluble residue, which consists of silica, is dried and weighed if desired.

*Iron* is estimated by neutralising 200 c.c. of the filtrate with sodium carbonate, boiling with an addition of ammonium acetate, and filtering, washing, drying, and weighing the resulting precipitate, which consists of iron oxide and alumina. On heating the filtrate from this last reaction with a little ammonium sulphide, *manganese* is thrown down and can be separated by filtration, washed, dried, and weighed in the usual manner. From the filtrate *calcium* is precipitated by ammonium oxalate, and, after removal by filtration, *magnesia* may be thrown down from the liquid by sodium phosphate. The amount of iron may be determined volumetrically in the original solution, and the resulting weight being deducted from that obtained by precipitation gives *alumina* by difference. To estimate *sulphates* 100 c.c. of the original solution are treated with barium chloride, the precipitated barium sulphate being weighed, and the amount of sulphuric acid found by calculation.

#### 4. Carbon.

Graphite (blacklead or plumbago) is a more or less impure form of carbon, occurring in irregular, blackish-grey, lustrous masses, which leave a black mark on the fingers or on paper, are greasy to the touch, and are easily converted into powder. The density depends on the degree of purity, varying between 2.08 and 2.50. In practice a sharp line of distinction is drawn between amorphous and foliaceous graphite, according to colour and covering power, the amorphous or purified form being the only kind referred to in speaking of the use of graphite in paints. Latterly, a maker of anti-

corrosive paints has taken to employing graphite in scales, analogous to the scaly oxides of iron. Before use the native article is purified by levigation and chemical treatment, the earthy impurities being removed by the former process, whilst in the chemical method the graphite is extracted with sulphuric acid and nitric acid, or by heating with potassium chlorate and sulphuric acid so long as fumes of chlorine are evolved.

Runge recommends stirring up the levigated graphite with sufficient concentrated sulphuric acid to form a thin pap, the mixture being then left to heat, and washed with water after a lapse of thirty-six hours. The manufacture of ferrous sulphate can be pursued in conjunction with this method of purification.

Purified graphite is entirely impervious to the influence of any acid whatsoever.

#### APPLICABILITY OF VARIOUS PIGMENTS AS ANTI-CORROSIVE PAINTS.

In previous sections the whole of the pigments employed in anti-corrosive paints have been dealt with, and it remains therefore only to consider their suitability for this particular purpose. It has already been mentioned that very divergent opinions prevail with regard to red lead and iron oxide in this connection, and the same may also be said of the pigments used as covering paints. One side champions the employment of lead paints (white lead), while another advocates zinc white, and a third upholds iron oxides as the best for anti-corrosive paints, a fourth party rejecting the latter pigments altogether, on the erroneous reasoning that iron oxide is itself iron rust, and must therefore necessarily engender rust. All, however, agree on one point, *viz* : That the pigments must be permanent, and even acid-resisting. Nevertheless, when the aforesaid pigments are tested, it is found

that only a single one out of the whole is really acid-resisting—all the others dissolving more or less completely in more or less concentrated acid. The sole acid-resisting pigment is graphite, this being the one least generally used—probably because of its dark colour.

Let us compare the opinions expressed with regard to the various pigments.

On the lead pigments in general—red lead excepted—Landolt says “These pigments, with few exceptions (chrome yellow), contain a basis of white lead. The usual additions for toning or adapting the pigments to various purposes being black mineral and vegetable colours, such as mineral black, vine black, lampblack and graphite; other toning colours being ochre, earthy colours and iron pigments. The barytes, chalk, etc., used for loading should not occur at all—except in minute quantities—in good paints for which normal prices are paid. The anti-corrosive paints with a basis of lead are put on the market under various names, such as diamond paint, silver-grey, metal-grey, iron-grey, etc. The general characteristics of this group of paints, when properly compounded, are: good covering power, durability, and capacity for resisting acids, though they exhibit a tendency to darken with age. They can be recommended where smoky fumes are prevalent.”

Simon says of the lead paints: “White lead forms an excellent pigment owing to its great adhesive and covering power, though it is readily darkened by exposure to sulphuretted hydrogen, and is subject to further chemical changes on account of which the coating of paint requires frequent renewal. As a bottoming paint for iron, white lead is inefficient, but when applied over a coating of red lead it answers fairly well, even for marine work. The principal defects of the lead pigments are to be sought in the readiness with which they decompose the varnish. With the same

rapidity with which oils and lead pigments saponify and—in the case of drying oils—produce very hard drying paints, proceeds the further decomposition of the vehicle, the originally elastic skin of paint becoming brittle and cracked through the formation of lead linoleate, which being crystalline causes the smooth, tough surface of the paint to change to a rough appearance. Already in three to four months' time crystals can be detected by the magnifying glass, and subsequently the lead linoleate is converted into brittle linoxyn, whereby the anti-corrosive paint is caused to crack and leave the underlying iron a prey to rust. This tendency is more particularly noticeable in varnish boiled with litharge, being less observable in lead-free varnish (manganese varnish), provided the pigment is also free from lead. In this case manganese linoleate, an elastic compound which only gradually changes into linoxyn, is formed, and it is not until eight or ten months have elapsed that recognisable traces of decomposition of the paint can be discerned by the glass."

According to Landolt, the zinc paint group as a rule take up more oil than the lead pigments. The following bodies are used as a basis: zinc white, zinc grey (by-product in zinc white manufacture), calamine—either ground alone or in combination with mineral bodies (silicates)—lithopone permanent white, zinc sulphide white. As regards the substances used for loading and toning these pigments, they are in both cases the same as those employed with lead pigments. The paints of this group are generally met with in commerce under the names: Platinum paint, Bessemer paint, silicate paint, or adamantine paint, and when properly compounded yield good results.

The general characteristics of zinc paints are good covering power and great durability—provided the constituents are properly compounded. The acid-resisting properties are

poor to good, according to the composition; the tendency to darken is but slight, and they can only be recommended for use wherever smoky fumes are not in question, unless the paint possesses good acid-resisting properties.

With reference to the use of zinc dust, *i.e.*, ground zinc ores, as a pigment for anti-corrosive paints, Spennrath states that "this application of the powder is no novelty, though a new name has been given to the material and it is now termed metal paint. Many years ago zinc dust was used as the pigment in the so-called galvanic paint, which mixture of oil paint and zinc dust was proposed as a substitute for coating iron with zinc by the galvanising process, it being assumed that the zinc would form a rust-preventing galvanic couple with the iron. The result was, however, failure, and the circumstances soon fell into oblivion. Now, zinc dust reappears on the scene as metal paint for which it is claimed as a predominant quality that hydrogen is liberated which in the nascent state, reduces rust to ferrous oxide or magnetic oxide, so that the paint is not merely rust preventing but also rust destroying. The experiments made to demonstrate such liberation of hydrogen prove nothing, since the gas in question can only be liberated by zinc when in contact with water, a condition impossible of fulfilment when the metallic pigment is ground along with linseed oil or a vehicle insoluble in water."

Spennrath says further that "at the instant hydrogen is liberated the zinc will have ceased to be in the metallic state and will be in the condition of oxide. To liberate 1 gram of hydrogen necessitates the consumption of 32 grams of zinc and their conversion into 40.7 grams of zinc oxide, which occupies just as much space as the metallic zinc from which it originated. Now it is claimed that the liberated hydrogen destroys pre-existing rust by converting it into ferrous oxide. Both ferric oxide and ferrous oxide are



compounds of oxygen with iron, the former containing 30 per cent. and the latter 22 per cent. of oxygen ; consequently to convert ferric oxide into the ferrous form it must be deprived of oxygen, an operation known as reduction, the active body therein being termed a reducing agent. When hydrogen reduces ferric oxide, it deprives the latter of oxygen, with which it combines itself to form water. This is, however, not the sole water which would make its appearance during the assumed action of hydrogen, iron rust containing 25.2 per cent. of chemically combined water ; and as the ferrous oxide formed from the rust cannot fix more than 20 per cent. of water there would be produced altogether about 15 per cent. of free water—calculated on the weight of the rust. Consider, now, what would happen on the conversion, in the manner described, of the rust underneath a coat of paint. The resulting water must find a way of escape, and would simply burst away the impenetrable paint. Moreover, the vaunted conversion of iron rust into innocent magnetic oxide of iron would be useless [reason not stated].”

The same authority also avers that “zinc dust has no greater durability than zinc white in paints for open-air use, the reasons for which may be readily gathered from the changes suffered by all zinc articles exposed to the weather. These soon become covered with a layer of zinc carbonate, the same would happen to zinc dust, the more readily on account of its fine state of division and the consequent incomparably greater amount of surface exposed than in the case of a smooth face of metal. The result is that the individual particles of the powder are not merely covered with a skin of zinc carbonate, but are entirely converted into that substance. What this implies will be more clearly evident from the following calculation : 65 grams of zinc produce 125 grams of zinc carbonate. Now, whereas the specific gravity of metallic zinc is 7.2, that of the carbonate

is 4.44; and hence, while 65 grams of zinc occupy a space of  $\frac{65}{7.2} = 9.02$  c.c., 125 grams of zinc carbonate occupy  $\frac{1}{4} \cdot \frac{3.5}{4} = 28.1$  c.c. In other words, metallic zinc increases in volume threefold during its conversion into zinc carbonate. It is easy to imagine what will happen when this conversion and expansion of the pigment goes on in an already dry and hard oil paint. What would be the fate of a wall of masonry if every brick were to expand on all sides at once?

"Zinc white is much more durable for indoor work, since, although carbon dioxide may be also present in the air of rooms, a necessary adjunct for the conversion of the metal into zinc carbonate—*viz.*, water—is here lacking, carbon dioxide having no action on dry zinc white. If an oil paint containing zinc dust, zinc white, or zinc grey, does not decompose in a few days when exposed to the air, no thanks are due to the stability of the pigment, but rather to the protective influence of the resinified oil enveloping every particle of the colouring matter. Even this protection is not permanent, and consequently the destruction of a zinc grey (zinc white) paint in the open air is a foregone conclusion."

(With regard to the incorrectness of this latter assumption, see p. 187.)

The iron group of paints is characterised by Landolt in the following terms. "This class comprises iron minium, colcothar, Venetian red, and the so-called scale armour ('Panzerschuppen') paints. Under no circumstances should they contain filling or loading substances, such as barytes chalk, kaolin, and the like. A distinction is drawn between—

"(a) Paints of predominating earthy-pigment character and pulverised amorphous basis, such as iron minium, colcothar, Venetian red, etc. When properly made they cover well and are durable, but not acid resisting.

"(b) Paints of crystalline character, such as the 'Panzer-

schuppenfarben ' (scale armour paints). These, when properly compounded, cover well, and form very durable acid-resisting paints."

According to Simon, " the iron oxides used, under various names—iron red, colcothar, *Caput mortuum*, etc.—in paints are inferior to red lead, especially for first coats on ironwork, requiring more frequent renewal, on which account they cannot be classed among the pigments for ' durable oil paints '. Exceptions to this rule are to be found in a rich iron minium containing 97 per cent. of ferric oxide, and a fine-scaled micaceous iron ore, which repeated tests have shown to be at least equal to red lead. By reason of their high covering power, which is eight to ten times greater than that of red lead, and the scaly nature of the micaceous ore, these two have been used for some years with advantage for bottoming on ironwork."

With reference to the use of iron minium in France, Balat remarks that the oxide obtained from Anderghem is occasionally used as a first coat on iron, but that the material is rarely obtainable pure, adulteration being so easy. Moreover, it is unsuitable for painting iron railway or road bridges, because of the soluble salts it forms with the sulphurous gases resulting from the combustion of coal in locomotive engines; whereas the compounds formed therewith by red lead are insoluble.

Mierczinski says: " Iron minium forms a strongly adherent first coating for subsequent coats of oil paint on iron, and on the score of economy is preferable to red lead for this purpose.

" The artificial iron oxides (*Caput mortuum*) are altogether unsuitable for preserving iron from rust; on the contrary, they facilitate rusting."

The following axioms are laid down, for pigments, by Landolt: " All colours used in the preparation of paints

for iron should possess a maximum of covering power and be chemically pure, so as to ensure proper distribution in painting. The selection of the colours should not—as so frequently happens—be made at random, but should be based on good theoretical grounds and on experience.”

Such are the divergent views on the suitability of the individual pigments for anti-corrosive paints. None of the pigments in use is capable of permanently resisting the action of acids, unless protected with an envelope of linseed varnish; and some of them (the lead pigments) must be credited with exerting chemical influence on the oil or linseed varnish. This action is confirmed by Mierczinski, who states that the good appearance of white lead is due to the contained hydroxide, which combines chemically with the oil to form a lead soap, dissolving in the surplus oil and constituting a kind of varnish, which covers the lead carbonate and imparts body and covering power thereto. So soon, however, as this lead soap is present in quantity the white lead loses in covering power and opacity, the paint becoming more or less transparent, horny, and brittle. According to Spennrath, zinc white undergoes decomposition by the action of atmospheric air; whilst in the artificial iron oxides the free acid present reacts on the varnish (and perhaps also on the iron itself at a later stage). In fine, there is no pigment but which may be subject to decomposition by some influence or other. Theoretically, therefore, none of these pigments is suitable for use in anti-corrosive paints, since the quality of resisting power is exacted of them. The author has never held such extreme views, but holds that selection should be made of some pigment either absolutely or relatively inert towards linseed varnish, a condition fulfilled by—

1. All zinc pigments.
2. All native oxides of iron.
3. Graphite.

Moreover, white lead should not be excluded, although, as we have seen, it enters into combination with linseed varnish. In accordance with the axiom expressed by the author and others, that in every paint each particle of pigment should be so enveloped in linseed varnish as to render it entirely independent of and secure from external influences, all the above-named pigments are admissible, and Spennrath falls into considerable error in asserting that zinc white suffers decomposition in the paint; in fact, in another part of his pamphlet he states that decomposition is precluded in pigments held together by linseed varnish.

Let us now examine the state of affairs in the case of inert bodies, which, like barytes, are indifferent towards all influences, even of the strongest acids. The adulteration of paints with barytes is objected to universally, without considering that this substance is an absolutely unalterable hard material, possessing only the single defect of low covering power. The author agrees that adulteration should be condemned, but he believes that no one has ever proved barytes to exert any injurious influence in paint; on the contrary, it is presumable that this substance must form a very solid paint, by reason of its own inherent hardness. However, barytes requires but a small quantity of linseed oil to bring it to a proper workable consistency as paint, and, moreover, it distributes very badly. Nevertheless it would seem advisable to institute extensive practical experiments with paints in which barytes could be associated with some pigment requiring a large proportion of varnish, such, for instance, as zinc white. The author is far from advising the employment of adulterants in pigments; but if it should be proved that barytes forms a suitable material for anti-corrosive paints, one would not be justified in discarding it for the sole reason that it is also employed for purposes of adulteration.

Having now ascertained which pigments are suitable for our purpose, we will next consider

## CHAPTER VI.

### THE INFLUENCE OF THE PROPORTION OF DRYING OIL ON THE DURABILITY OF THE PAINT.

IN the preparation of oil paints use is made partly of raw linseed oil and partly of linseed varnish—either in the natural state or bleached—and each separate class of pigment requires, according to its properties, different quantities of the afore-said liquids in order to become converted into the condition of an oil paint. Thus, for example, lead pigments, especially red lead and white lead, require considerably less linseed oil or varnish than do certain other metallic pigments—*e.g.*, zinc white—while all the earthy colours, particularly ochre, umber, certain iron oxides and the like need a considerable amount of liquid to convert them into paint. Moreover, the individual pigments themselves vary in their requirements of oil; so that in the case of zinc white (and also white lead) fluctuations in this respect of as much as 10 to 15 per cent. occur. This divergence in the oil consumption of the various natural and artificial pigments is attributable to the form of the individual particles of the colouring matters, hard particles of crystalline nature requiring to be ground to paint a much smaller proportion of oil or varnish than the soft, amorphous pigments. Barytes affords a decisive instance of this, also in the case of earthy pigments the consumption of oil increases proportionally with the softness and absorbent nature of the substance, a soft argillaceous ochre, for instance, requiring much more than a sandy ochre or heavy iron oxide. As a general rule it may be said that all the specifically heavy pigments, *i.e.*, all such as occupy but little space, require a much smaller quantity of oil or varnish than such as are voluminous; hence bulk of itself affords a criterion of the requirements of

a pigment in respect of oil. These facts are well known to paint manufacturers and experienced master painters, and the author only refers to them here in order to attract the attention of a wider circle on the one hand, and on the other to utilise them as a basis for further remarks.

We know that all paints are the better able to resist atmospheric influences, rain, snow, cold and heat—as well as the mechanical effects exerted by sand and dust in conjunction with the wind—in proportion to their elasticity. A coating of best carriage varnish exhibits far greater powers of resistance than one of cheap copal varnish; and when the reason for this superiority is investigated it is found that the former varnish contains the much higher proportion of oil. It is an established fact that all varnishes rich in oil are more resistant than such as are poor in that constituent, and it is equally established that this superiority is actually due almost exclusively to their higher content of oil.

What, now, is the state of the case with regard to the influence of the oil ratio on the durability of paints? It has been shown that some pigments require only a small quantity of oil, chief among which may be classed the lead compounds, white lead and red lead, these forming a fairly thin paint with 12 to 15 per cent. of a drying oil, whereas zinc white requires about 30 per cent.

Similar conditions obtain in respect of all other colours, and it is worth while to consider in what manner they manifest themselves in the resulting paints.

If we apply a given weight—say 1 kilo—of a heavy pigment over a given surface, we find that it does not cover so large an area as the same weight of a specifically lighter pigment, because the former is less bulky than the latter. Assuming the volume of the lighter pigment to be double that of the heavier kind, the former will then cover twice as much surface, the volume for a given weight being the criterion of covering power.

For example, if 200 parts, by weight, of oil are used with 1000 parts by weight of one pigment, whilst the same weight of another (lighter) pigment requires 700 parts of oil; and also assuming that the volume of the latter pigment is as large again as that of the heavier kind, then approximately

1200 parts by weight or 700 volumes of the heavy paint contains 200 parts of oil.

1700 parts by weight or 700 volumes of the lighter paint contains 700 parts of oil.

1200 parts of the latter would contain 500 of oil.

Consequently, if 1 part by weight of the lighter paint will cover a surface as great as that covered by 2 parts of the heavier kind, the relative quantities of oil on a given area will be 20 : 25.

Of course this is only a hypothetical example, the differences will mostly be much smaller in practice. In any case the old axiom holds good, *viz.*, the larger the proportion of drying oil taken up by the pigment to form a workable paint, the more durable will the resulting coating of paint prove. This is also confirmed by practical experience, for it is an undoubted fact that paints made from white lead or red lead perish much sooner than those made of zinc white or ochre, the gloss and elasticity disappearing much quicker and leaving the pigment in a shorter time in a condition in which it can easily be scraped off as powder or in flakes.

Attention was bestowed by Mulder on the ratio between pigment and vehicle, and he came to the conclusion that a portion of the red lead exerts a drying influence on the linseed oil, whilst the remaining and far larger quantity should be regarded as a by no means unconditionally essential loading or ballast.

One hundred parts of linseed oil are ample for binding 9 parts of lead oxide; so if for the sake of convenience we say 10 parts, then to each 1 part of linseed oil there will be  $\frac{1}{10}$  part of lead oxide.

To prepare a free working paint from white lead or red lead, 35 to 40 parts of oil are necessary to each 100 parts of



ground pigment. Of these, however, the aforesaid quantity of oil only binds 4 parts, leaving 96 parts unaltered and simply enveloped in the oil, to act as covering material. The question now arises spontaneously. Cannot a few of these 96 parts of white or red lead be replaced by a neutral substance without endangering the utility of the whole, and may not such neutral substance, when obtained by grinding a very hard and durable material possibly exert a favourable influence on the durability of the paint? Some very important experiments in this direction were made by Mulder with mixtures of red lead and Anderghem iron oxide, ground roofing tiles, clay ironstone, hæmatite, magnetic iron ore, and ground slate. He reported that: 100 parts of commercial boiled linseed oil, with 2·6 per cent. of lead oxide, made up into paint with—

5 parts of red lead to 40 parts of Anderghem iron oxide,  
or 25 " " " " 40 " " "

gave very satisfactory results, especially in the proportions 25 : 40

The same, with—

20 parts of red lead to	} 100 parts of Anderghem iron oxide
40 " " "	
65 " " "	
90 " " "	
120 " " "	

also behaved well, no difference in covering power being noticeable.

The same, with—

20 parts of red lead to	50	} parts of red roofing tile powder;
40 " " "	50	
65 " " "	50	
90 " " "	50	
120 " " "	50	
120 " " "	100	

covering power satisfactory in the higher proportions.

The same, with—

20 parts of red lead to	} 100 parts of clay ironstone;
40 " " "	
65 " " "	
90 " " "	
120 " " "	

covering power satisfactory in the higher proportions.

The same, with—

20 parts of red lead to				} 100 parts of hematite,
40	"	"	"	
65	"	"	"	
90	"	"	"	
120	"	"	"	

covered excellently.

The same, with—

40 parts of red lead to				10 parts of magnetic iron ore,
40	"	"	100	" blue bricks,
40	"	"	100	" ground slate,
40	"	"	100	" roofing tile,

covered admirably.

"I will postpone," says Mulder, on 5th March, 1865, "a final decision on the behaviour of these paints with regard to adherence, hardness and resistance to wind and weather, they being still too young to enable a judgment to be formed. This much, however, I may say, that a large number of them seem to attain the maximum degree of hardness. This is satisfactory, and I am of opinion—from these few simple experiments with boiled linseed oil and materials almost valueless in a pecuniary sense—that for imparting hardness and covering power to paint, leaving colour out of the question, one need seek no farther than ground roofing tiles, old blue bricks, or burned clay ironstone, and may leave all secret preparations alone in future."

A few of the preceding paints were too thick, others too thin; it is, however, worthy of note that all of them, irrespective of consistency, adhered satisfactorily to iron.

The strips of sheet iron used were all painted on one side only, and then exposed for some months to wind and weather, rain and sunshine. The unpainted side was found covered with rust in all instances; but no trace of rust or peeling was observable on the painted sides.

Where no decorative effect is required, many conditions can be dispensed with in the paint; but the following three essentials must be maintained;—

1. The linseed oil must be well boiled, well prepared, of good quality, and contain 2 to 3 per cent. of lead oxide.

2. The ground pigment must contain an addition of lead oxide; red lead is believed to be the best, but the minimum amount has still to be determined. In the brief space of time occupied by the experiments no difference in point of hardness and durability could be detected between the paints rich and poor in this constituent.

3. A hard, inert powder, ground as finely as possible, may be added, the quantity being limited by the workability of the paint.

As a matter of fact the present communication contains nothing novel, it being an old practice to strew sand over the newly painted surface after applying the final coat, when the production of a durable coating is the sole consideration. Nevertheless, this useful method is too little known.

From what has been said hitherto with regard to pigments there is no difficulty in determining which are the most suitable; and it is also easy to draw the following conclusion, *viz.*, that "security for the production of a suitable anti-corrosive paint, conforming to all necessary requirements, is afforded by the use of such pigments as are as far as possible inert and require a large proportion of linseed varnish in order to form a workable paint".

It also follows from the particulars given that inert bodies that are not pigments—*e.g.*, barytes, brick dust, and various other materials—may form part of anti-corrosive paints, provided they consume a large proportion of varnish and are in a sufficiently fine state of division to yield a smooth, non-granular product. To prevent fraud, it will then be the business of paint buyers to come to some agreement as to the suitable prices for such specially compounded paints. The author would repeat that he has no desire to treat the addition of such materials as an adulteration, so far as it has been

shown that they act as well as or better than the more expensive pigments. At present, ground slate already frequently forms a constituent of anti-corrosive paints without being regarded as an adulterant<sup>1</sup>. Actually, no closer definition of adulteration is needed than "the addition of inferior materials to paints sold as 'chemically pure'". If this assurance is not given, then the price charged must be taken into account before one can regard these additions as adulteration, and on this point an opinion has already been expressed (p. 116).

NOTE—Mr J. Cruickshank Smith, in a paper read before the Paint and Varnish Society on May 18, 1911, said. "Brief reference must be made to one of the most recent developments in connection with scientific paint-making, namely, the use of 'inhibitive pigments'. This term has arisen out of researches (chiefly those of Cushman and Walker) connected with the electrolytic theory of corrosion, and attempts have been made to prove that pigments can be grouped in classes according as they tend to prevent or inhibit corrosion, to accelerate corrosion or are inert in this respect.

"It is well to point out that certain conclusions which have been arrived at in respect of such recognised inhibitors as potassium bichromate, chromic acid, and caustic soda are not relevant to the problems attending the protection of iron and steel by means of oil paints, for the reasons that none of these chemicals are or can be constituents of such paints and that they act only in watery solution, and the presence of moisture must be rigorously guarded against in paint. A further difficulty has been introduced through Friend<sup>1</sup> having shown in his recent researches that the effect of an inhibitor depends on the concentration of the solution, and that as the concentration varies the action may be reversed, the inhibitor becoming an accelerator of corrosion. The study of pigments (using that term in its strict technical sense, which connotes insolubility) in relation to their effect as inhibitors of corrosion has not so far been sufficiently exhaustive or long continued to permit of entirely satisfactory deductions being drawn. While it is unsafe, therefore, at present to claim very definitely for any pigment, under the conditions to which it is exposed in a paint film on iron and steel, unfailing action as an inhibitor of corrosion or even assert with any degree of certainty what pigments will be uniformly inert in this respect, signs are not wanting that we can with a growing degree of confidence point to certain pigments which act as accelerators of corrosion, and these should be rigorously excluded from protective coatings."

It is quite true that in many of the experiments on the prevention of corrosion of iron and steel most of the solutions employed were aqueous solutions of various chemicals. In the case of a paint film the pigment is surrounded on all sides by a varnish through which very little water can penetrate so that the conditions are very different, any inhibiting action there might be not having free play, still it seems that certain pigments, *e.g.* American vermilion, a basic chromate of lead, have a decided inhibiting action.

<sup>1</sup> Paper before the Iron and Steel Congress, May, 1911.

## CHAPTER VII.

### THE PREPARATION OF ANTI-CORROSIVE PAINTS

THE compounding of paints is a fairly simple operation, consisting simply in the mixing of the finely divided pigmentary substance with the linseed varnish, grinding the two together in a paint mill, and finally thinning the product down with linseed varnish to the proper working consistency. All pigments, even varieties of the same pigment, require varying amounts of varnish in order to produce paints of definite con-



FIG. 51.—Paint-mixing machine.

sistency, therefore exact details cannot be given. The consistency of the varnish also influences the result, the thicker grades being proportionally less able to take up pigment, and at the same time producing correspondingly more viscous and therefore less workable paints. Hence stress must be laid on the attainment of uniform strength in the linseed varnish, to which and occasional tests should be made with the viscosimeter. Thinning down the paint with turpentine

should not be resorted to, since this treatment diminishes the proportion of linseed varnish, the paint then being rendered less durable. Neither should driers be added in any form, but the varnish should possess in itself sufficient drying power to make such additions superfluous. Liquid driers in particular, by reason of their richness in lead compounds, are very unfavourable to the durability of the paint, causing premature decay

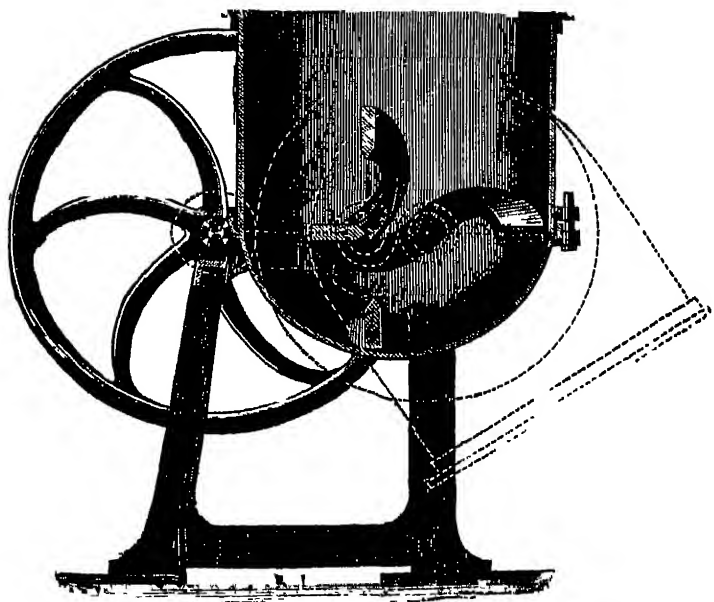


FIG. 52.—Paint-mixing machine.

The author has no intention of giving a string of recipes for anti-corrosive paint, but will deal generally with the operations of mixing and grinding, mentioning several mechanical appliances for these purposes that have behaved well in practice. In a subsequent chapter will be found sundry particulars relating to various paints in current use.

In addition to the qualities already specified, the pigments employed must be perfectly dry and in the finest pos-

sible state of division. They are placed in a suitably large vessel containing the linseed varnish, where the two are mixed intimately together by means of a stirrer. For large quantities, such as are generally employed in the preparation of anti-corrosive paints, hand mixing is too cumbrous, tedious and costly, it is advantageously superseded by mechanical appliances, such as that shown in plan in Fig. 51, and in vertical section in Fig. 52.



Fig. 53.—Paint mixer.

In this smooth-walled mill two twisted annular beaters, engaging one with the other, rotate in opposite directions, ensuring the intimate admixture of the materials in a comparatively short time, and with less expenditure of power, than could otherwise be effected. The action of the machine proceeds with great uniformity, resulting in the production of a satisfactory effect, the particles of material kept in continual motion being forced to intermingle until worked up into a homogeneous mass. The stirrers brush against the

bottom of the mixture and against each other at every revolution, thus preventing any part of the mass from remaining unacted upon. The machine is emptied by simply tipping the pan, the stirrers being kept in motion in order to facilitate the removal of any material adhering to the sides. To clean the machine out thoroughly it may be taken apart by simply removing a cotter.

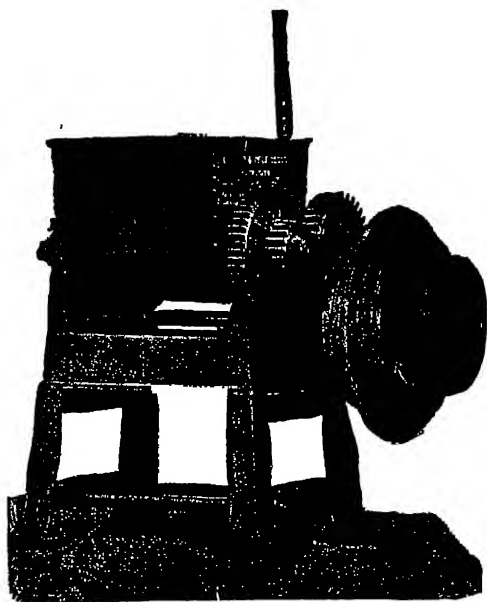


FIG. 54.—Paint mixer.

The mixer of Messrs. Werner & Pfeiderer (Figs. 53, 54) is extremely simple in principle, and unsurpassable in efficiency. It is made in various sizes, to treat from one cwt. to a ton and a half of paint, the quantity each mill is capable of dealing with at a time being not merely dependent on the specific gravity of the materials, but also to a large extent on the consistency and other properties of the mass. In most cases the stronger machines are also suitable for dealing with



smaller quantities than their normal capacity, but it is better to state the purpose for which the mixture is required when ordering. When the machine is in motion the kneading paddles work one against the other inside the mixing pan. To save time and increase the effect, the motion should be reversed at intervals, the machine being fitted with reversing gear for that purpose. The best results are obtained when the amount in machine is such that the peculiar sound of the materials dashing from one paddle to the other can be heard when the apparatus is in motion, an effect generally obtained when the amount of dry material is just enough to completely cover the paddles. The pan can be tipped for emptying, the smaller ones being so constructed that they can be dismantled to facilitate cleaning, the trough being taken apart and the paddles removed.

The preceding appliances, whilst intimately mixing the varnish and pigments together, have no effect on the fineness of division of the latter. Consequently the product is lumpy, and although the lumps can be broken down with the hands or by a muller and stone slab, the paint does not yet exhibit that fine and soft salve-like mass characteristic of the perfectly ground article.

To bring it into this condition further treatment is required, consisting of an intimate mixing, crushing, and so forth, performed by hand in the case of small quantities, but necessitating the employment of properly constructed paint mills when the work is performed on a large scale.

Paint mills may be divided into three classes, according as the grinding of the material is effected—

- (a) Between two conical, roughened surfaces, one fixed and the other executing a rotary movement ;
- (b) Between two flat grooved plates, moving eccentrically in opposite directions ; or

(c) Between a series of rotating steel, porphyry (granite), or porcelain rollers.

For works of moderate size the mills of class *a* are suitable, but larger quantities can only be dealt with by roller mills (class *c*).

Fig. 55 shows a funnel-shaped or conical mill, the upper grinding surface of which is attached to the fixed feed hopper, whilst the movable lower conical grinding surface is adjusted

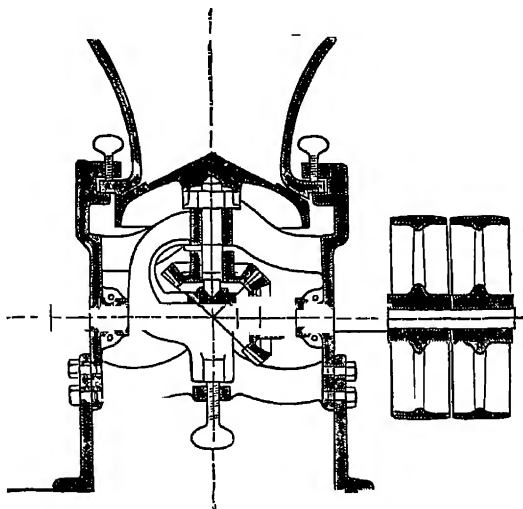


FIG. 55.—Paint mill with conical grinding surfaces. (For power.)

by a screw and spindle so as to leave merely a small aperture for the outflow of the ground paint. The conical surfaces must be accurately turned, the actual grinding surfaces forming only a portion of the funnel or cone, which portion is in both cases riffled in order to increase the grinding power. The riffles run from the centre towards the edge, which, however, they do not quite reach.

The paint to be ground is placed in the hopper, and on issuing from the mill is conducted into a receptacle below by means of a scraper placed at the side.

The larger mills are always of the roller type, such as illustrated in Figs. 56 to 58 They contain from three to

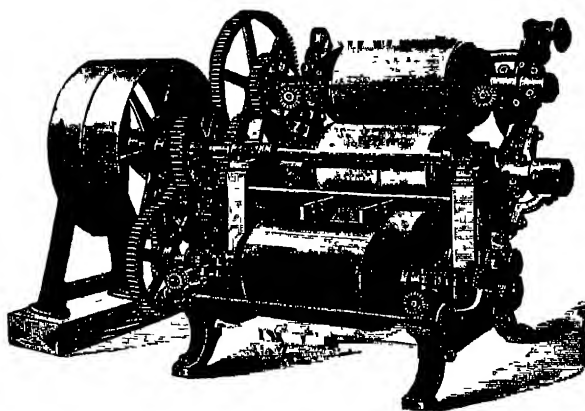


FIG. 56.—Triple-roller paint mill.

six rollers of equal dimensions, mounted one above another or side by side in a strong frame, and caused to rotate at

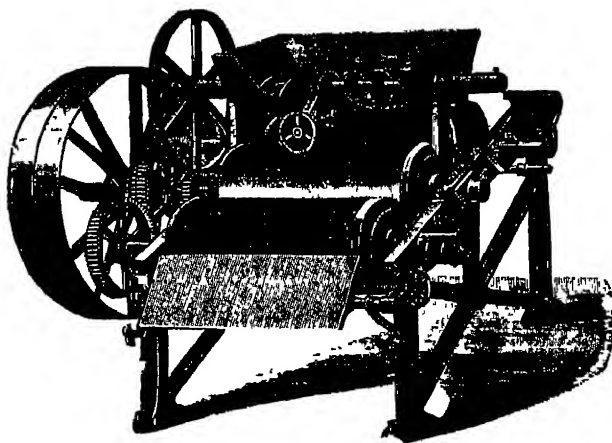


FIG. 57.—Quadruple-roller paint mill.

different speeds. The lowermost roller generally executes a lateral motion as well. The mixture of oil and paint to be

ground is fed between the first pair of rollers, being prevented from running away over the ends of the rollers by a hopper. On issuing from these rollers, where it receives the first grinding, it is carried over by surface adhesion to the second pair (Nos 2 and 3), being reground between these. From the third roller it is removed by an adjustable scraper, and

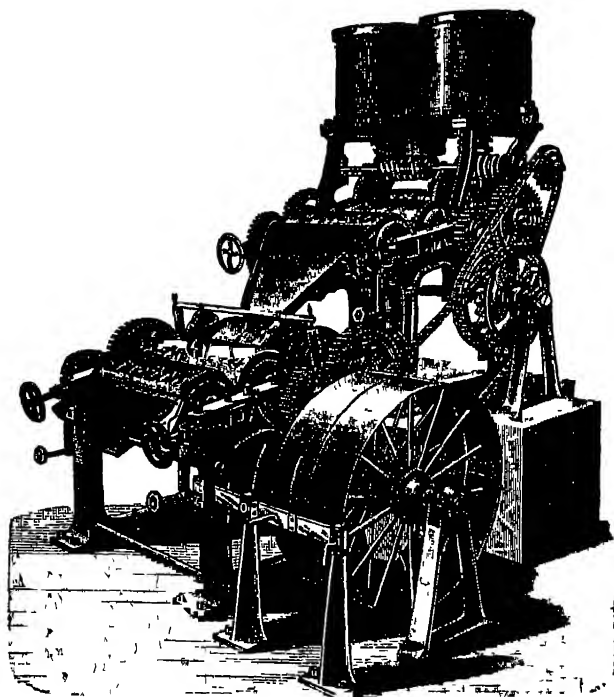


FIG. 58.—Combined triple-roller mill and mixer.

if not sufficiently fine is afterwards passed through the mill a second, or even a third time, the rollers being meanwhile set closer together by the adjusting screws.

Fig 58 shows a combined mixer and grinder, the pigment and varnish being placed in the mixer—at the top of the apparatus—passing from thence to the mill proper below.

The finished paint must be in a sufficiently finely ground condition and of a proper workable consistency—unless made extra strong, to be afterwards reduced by the consumer—and it should be protected from skinning, both during manufacture and storage

## CHAPTER VIII

### ANTI-CORROSIVE PAINTS

#### *Graf & Co.'s Panzerschuppen (Scale Armour) Paint*

(According to the cancelled patent specification)

A patent was applied for in respect of a paint for boilers, the mixture consisting of scaly micaceous iron (specular iron ore) and linseed varnish, its object being to facilitate the removal of boiler incrustation. The use of any fine varnish free from acid or alkali was contemplated, in conjunction with a mineral pigment of scaly structure resembling native graphite in appearance, and containing the following constituents.—

Silica . . . . .	5.40	per cent.
Phosphoric acid . . . . .	0.05	"
Iron oxide . . . . .	88.68	"
Alumina . . . . .	0.40	"
Manganese protoxide . . . . .	Trace.	
Cobalt and nickel protoxide . . . . .	0.12	"
Lime . . . . .	1.78	"
Magnesia . . . . .	1.88	"
Alkalis and loss . . . . .	0.85	"
Water, carbon dioxide, and organic matter . . . . .	1.99	"

The silica and phosphoric acid were in combination with iron oxide, and the small quantity of carbon dioxide apparently combined with the lime and magnesia. No sulphur or sulphur compounds could be detected. The applicant reserved the right to modify the percentage content, and to make small additions of other more subsidiary substances.

The intention was to coat the interior of the boiler with

the paint, which, from its composition and behaviour in practice, was claimed to be unalterable and irremovable under the influence of heat. Moreover, it was said to be insusceptible to the action of either hot, cold, or salt water, and to in no wise reduce the conduction of heat. The paint, having been previously well stirred up and reduced with best linseed varnish, was to be laid on as thinly as possible, so as to just cover the metal, this treatment being repeated as often as necessary to produce the desired thickness of coating, and each layer being allowed to dry properly before applying the next one. The use of suitable quick-drying varnish to accelerate drying was also contemplated.

In place of powder the pigment was in the form of foliaceous scales, and it was claimed that these scales overlapped one another in the paint, attaching themselves so firmly to the boiler plate that on the one hand no unforeseen loosening of boiler incrustation could occur, whilst on the other hand this loosening could be easily effected in the operation of cleaning out the boiler.

The further advantage claimed for the use of this paint for the interior of boilers was protection from rust or other form of corrosion.

#### *Lender's Anti-corrosive Paint.*

This preparation is intended for the preservation of iron from rusting or attack in any other way, it being stated to be impervious to heat, cold, and the action of acids. When tested on iron plates it was found to resist warm water and steam, volatile acids, alkalis, gaseous ammonia, hydrochloric acid gas, and sulphuretted hydrogen gas.

The principal constituent is a silicate of iron found in the vicinity of deposits of iron ore and also as veins in granitic rocks weathered by exposure to the air. The composition of this finely divided material is as follows :—

Silica . . . . .	5.40 per cent.
Phosphoric acid . . . . .	0.05 "
Iron oxide . . . . .	88.56 "
Native alum . . . . .	0.50 ,
Lime . . . . .	1.75 "
Magnesia . . . . .	1.85 " "
Undetermined . . . . .	2.90 "
	<hr/> 99.91

It is sold in the form of a paste, finely ground in admixture with oxidised linseed oil or varnish, and, before use, is to be reduced with good linseed oil, together with an addition of driers, such as litharge, etc., if considered necessary; any mineral paint of a particular colour can be added to produce the desired tone.

#### RESULTS OF THE EXAMINATION OF SEVERAL ANTI-CORROSIVE PAINTS.

##### 1 *Bessemer Paint*

The pigment contains barytes, alumina, iron oxide, lime, silica, zinc oxide, sulphuric acid, carbon dioxide, and phosphoric acid. When treated with hydrochloric acid it evolves sulphuretted hydrogen. Graphite or other carbon is used as colouring matter, and linseed varnish as the vehicle, turpentine probably constituting the drier. The presumptive constitution is therefore:—

Lithopone, or siliceous calamine ore, containing barytes and chalk, together with graphite or other form of carbon, and linseed varnish (with probably turpentine as a drier).

##### 2 *Diamond Paint.*

The pigment consists of white lead mixed with barytes, graphite or other form of carbon being employed for toning, and linseed varnish as the vehicle. No rosin, rosin oil, driers, or turpentine could be detected.



The paint is therefore compounded of barytes, white lead, graphite, and linseed varnish.

### 3. *Diamond Paint.*

The pigment is white lead, giving an iron oxide (ochre ?) reaction. Ultramarine, mixed with graphite or other carbon, is used for toning. No rosin, rosin oil, driers, or turpentine were found.

Constitution: white lead, probably with a little ochre, ultramarine, graphite, and linseed varnish.

### 4. *Durable Paint.*

The pigment is an earthy, granular, finely powdered substance, giving reactions for zinc oxide associated with silica, phosphoric acid, iron oxide, lime, manganese, and a little alumina. An addition of hydrochloric acid causes the evolution of sulphuretted hydrogen. The toning materials are ultramarine, graphite, or other forms of carbon, and the vehicle consists of linseed oil, neither rosin oil nor turpentine being present.

The presumptive constituents are: zinc oxide or calamine, ultramarine, graphite, and linseed varnish

### 5. *Iron Oxide Paint.*

The pigment contains iron oxide with a small amount of clay and pyrites, which gives off sulphuretted hydrogen when treated with hydrochloric acid. We have in this case to do with an iron oxide, presumably the residue from the roasting of pyrites. The vehicle is linseed varnish.

The paint is therefore composed of: iron oxide—contaminated with clay and pyrites—and linseed varnish.

### 6. *Armour-scale ("Panzerschuppen") Paint (Swiss origin).*

The principal constituent of the pigment is a granular reddish-brown iron oxide, somewhat greasy to the touch, and

interspersed with scaly, foliaceous, crystalline particles. No rosin, rosin oil, turpentine, or driers could be detected, and consequently the paint consists of—

Weathered micaceous iron ore and linseed varnish.

7. *Armour-scale Paint (German).*

The pigment is mainly composed of fairly dark grey crystalline, scaly, smooth, and greasy particles of iron oxide, interspersed with finely divided red iron oxide and a small proportion of gangue. A small quantity of graphite is present as colouring matter, the vehicle being formed of linseed varnish alone, no rosin, rosin oil, driers, or turpentine being present.

Constitution: micaceous iron ore—with a little graphite and gangue—and linseed varnish.

8. *Armour-scale Paint (Swiss).*

The bulk of the pigment is granular iron oxide, leaving a reddish-brown mark, intermingled with a relatively small proportion of foliaceous, scaly, crystalline, soft and greasy iron oxide, and a little gangue. Vehicle: linseed oil, free from rosin, rosin oil, turpentine, or driers.

The paint therefore consists of strongly weathered micaceous iron ore (with a little gangue) and linseed varnish.

9. *Armour-scale Paint (Swiss).*

Pigment principally finely divided reddish, earthy, smooth and greasy iron oxide mixed with crystalline scaly particles and a little gangue. Graphite occurs as colouring matter; and linseed varnish as vehicle. No driers, rosin, rosin oil, or turpentine.

Constitution: finely powdered, reddish, granular micaceous iron ore, interspersed with scaly particles and a small quantity of gangue, graphite in small amount, and linseed varnish.

10. *Armour-scale Paint (Swiss)*

The main body of the pigment consists of a somewhat finely ground, grey, smooth and greasy, crystalline scaly iron oxide intermingled with a little gangue. Linseed varnish forms the vehicle, and a little graphite occurs as colouring matter. No driers, turpentine, or rosin oil are present.

Constitution · moderately finely ground grey, scaly, micaceous iron ore, a little graphite, and linseed varnish.

11. *Platinum Paint.*

The pigment is chiefly zinc oxide, with an admixture of a greyish-black, granular substance giving reactions for silica, phosphoric acid, sulphuric acid, carbon dioxide, lime, magnesia, manganese, alumina, and lead, and giving off sulphuretted hydrogen under the influence of hydrochloric acid. No rosin, rosin oil, driers, or turpentine could be detected, the vehicle being composed solely of linseed varnish. Consequently the paint is compounded of non-barytic lithopone white, and linseed varnish.

12. *Platinum Paint.*

Pigment mainly composed of zinc oxide, with a little lead sulphate. Physical appearance and reactions similar to No. 11, sulphuretted hydrogen being also liberated on the addition of hydrochloric acid. Ultramarine is present as a toning material. Vehicle. linseed varnish, free from rosin, rosin oil, driers and turpentine.

Constitution · lithopone white, a little ultramarine, and linseed varnish.

13. *Grey Paint (German).*

The pigment is white lead shaded with ultramarine and a little graphite (or charcoal). Small quantities of alumina,

iron oxide, and soda were found. Vehicle—linseed oil, with a large proportion of resin and turpentine.

Constitution : white lead with a little ochre, ultramarine, resin dissolved in turpentine (amber varnish), and linseed varnish containing lead.

Comparative experiments have been made by Heyl with platinum paint, zinc paint, silicate paint, and graphite, with the following results :—

1. Platinum paint and red lead form a perfectly hard mass from which the linseed oil no longer volatilises.

2. Iron oxide, zinc paint, and silicate paint remain soft, so long as the linseed oil is not completely volatilised, but continue to lose body through the volatilisation (?) of the linseed oil, until eventually nothing is left but the uncovered powder, which then washes off in course of time.

3. Graphite and the mixed paints part with their linseed oil much quicker than those named in class 2, consequently the washing away of the residual powder will be effected much more rapidly, unless this latter is endowed with a special degree of adhesion towards iron, a condition that has not hitherto been observed.

#### PAINTS FOR SHIPS' BOTTOMS.

##### *(Anti-fouling Compositions.)*

These preparations have for a considerable time played an important part in England, owing to the recognised necessity for maintaining ships' bottoms in good condition, though it is only within the last few decades that data have been collected as to the effect of marine animal and vegetable incrustations, below the water line, on the speed and coal consumption of the vessel.

According to W. Hummel, the demand for special paints for ships' bottoms dates from the introduction of iron and steel into the art of shipbuilding. Wooden vessels are not

liable to become rusted, and ships of this class are protected from the accumulation of marine plants and animals by means of copper, or copper and zinc, sheathing. The same treatment has also been applied to iron vessels, but is only used when the ship cannot be docked for cleaning except at long intervals. So far as painting the ship's bottom with red lead, white lead, iron oxide, or zinc white is concerned, these materials are altogether inoperative against the vitality of the incrusting organisms, nor do they prevent the iron from rusting. The use of red lead as a first coating for steel ships was also abandoned on the fact becoming known that lead preparations are converted by sea water into lead chloride, which in contact with iron produces iron chloride and lead—the latter forming with the iron a strong galvanic couple productive of further corrosion.

Of the organisms growing on ships' bottoms, but little danger is to be anticipated from seaweed, these plants usually growing on the water line alone, since air is necessary to their development. The speed of the vessel is mainly checked by testaceous incrustations, which organisms are, as a rule, motile in their earlier stages of growth only. The task of the poisonous substances in anti-fouling compositions is therefore to destroy the vitality of the germs of such organisms remaining adherent to the ship's bottom. During a voyage the layer of paint is so far softened, under the influence of friction and sea water, as to enable the saline constituents of the latter to gain access and react on the poison in the paint, the result being the production of an antiseptic solution which kills the organisms attached to the surface of the vessel.

In tropical waters the rate of increase of these creatures is so rapid at certain seasons that the antiseptic material appears to be soon exhausted, the paint then ceasing to be capable of preventing incrustation.

When the vessel is laid up in harbour, incrustation progresses at a greater speed than during the voyage, the efficiency of an anti-fouling composition therefore depending mainly on the length of time the paint can continue to liberate an active antiseptic substance when the ship is laid up. In harbour, however, the surface of the vessel is not subjected to friction, consequently the antiseptic material in the outer layer becomes exhausted within a few weeks, and it is only after the spent outer layer has been removed by the friction engendered by the motion of the vessel, on the renewal of the voyage, that a fresh surface impregnated with toxic material is exposed. It is therefore possible under certain circumstances for a newly painted ship to become more thickly incrustated than one carrying an older coating of composition. Prolonged exposure of the fresh paint to the air considerably diminishes its anti-fouling power.

The records of the English Patent Office contain a large number of specifications of anti-fouling compositions, the earliest inventor of such preparations for preventing damage to ships' bottoms from the putrefaction of the wood, attacks by maggot, etc., being William Beele, who in the year 1625 patented a "cement" for protecting ships from the ravages of barnacles. This process consisted in boiling together a mixture of "wildfire" or gunpowder, water, cement, and "dressing for ships"; but as the composition of the latter items was not given, beyond a remark that they were extracted from certain minerals found in England and Wales, the real active agency was left unrevealed. In the same century Philip Howard and Francis Watson occupied themselves with the same problem, and, in their patent taken out in 1670, proposed pitch or resin as a preventive agent. In another specification, the same inventors describe a varnish of beeswax, turpentine, and granular lac dissolved in corn spirit. Two patents in 1670 and 1737 remained

uncompleted; and Emerton proposed to coat the hull with boiled oil of gelatinous consistency and containing compounded poison, pulverised glass, sand and dust, worked up along with paint and oil to a thick mass, this being then topped with a coat of thick oil paint.

A special report on a patent granted in 1754 refers to a mixture of clarified turpentine and distillation products from pine wood. At that period tar and lampblack appear to have played a leading part in all black paints for ships' use. One inventor, towards the end of the century, proposed to mix tar and iron filings, and to distil from the mixture a Japan black for masts and a thin tar for the hull. In 1791 William Murdak took out a patent for a paint compounded as follows: Iron sulphide was roasted, in air, along with zinc, the resulting yellow powder being mixed with turpentine or other vehicle. The presence of arsenic in the iron sulphide formed an important means of protection against incrustation by marine animals.

After this epoch a long period of inaction in this class of inventions set in, during which nothing worthy of record was proposed. Most anti-fouling compositions of a later period contain salt of mercury, which forms an excellent preventive of incrustations of marine animals; still more recently Baron Wetterstedt proposed to coat vessels with an antimonious lead preparation, the parts below the water line being covered with an amalgam of 17 parts of mercury, 2 parts of lead, and 1 part of antimony. Lead appears to be a particularly suitable means for the purpose in view.

The idea of an amalgam was taken up again in 1841 by Robert Mallet, for application to iron, which by that time had come into use to replace wood in ships' hulls. The invention consisted in the use of a double salt of zinc, or manganese, and ammonia, for cleaning and applying a coating of metal—zinc, mercury, and potash or soda—which

amalgam was covered with a protective layer of varnish, topped with poisonous paint. Palladium was also proposed as a coating, but, judging from the price of the metal, its use could hardly have been seriously contemplated. In 1848 Charles Hancock proposed gutta-percha, boiled in a solution of calcium chloride, and kneaded with a mixture of borax and shellac; while shortly afterwards two inventors proposed to use solutions of gutta-percha in benzol, a similar solution being also proposed in 1851, as well as on many subsequent occasions.

Arsenic first made its appearance as a poisonous constituent of anti-fouling compositions in a preparation of carbonate of iron and white arsenic, associated with coal-tar pitch and benzol, and from that time onwards was always used in conjunction with mercurial compounds. In 1852 the arsenical lead compounds, realgar and orpiment, and various arsenical salts were substituted. Two years later, Westwood and Baillie used white arsenic as an external layer, the novelty of their process consisting in the employment of the strongly adherent body asphaltum as a first coating on the metal surface.

In 1855 Greenhow put forward an entirely new proposition for the prevention of incrustation, in that, instead of applying a poisonous composition to the ship's bottom, he provided the latter with a perfectly smooth surface on which the marine animals could obtain no foothold. This was effected by coating the iron plates with a mixture of glass, resin, and soda (apparently a kind of enamel). In 1856 it was proposed to use a mixture of coal-tar creosote, insoluble lime soap, and copper oxide; and in the next year one inventor brought forward a project for killing all animal and vegetable incrustations by means of strychnine or atropine as an adjunct to anti-fouling compositions. The process of M. Crae (1858), in which bone fat and salts of



copper were employed, was not very durable, owing to the removal of the fat in course of time by attrition.

Hay's invention (1861) was intended for treating copper oxide in such a manner as to secure uniformity in the application of the paint. He precipitated black copper oxide from solutions of copper salts, and boiled the product in linseed oil, whereby the oxide was reduced forming a paint with the oil, a little silver or other metal or oxide being added to the preparation. Another patent prescribes the use of asafoetida, antimony, mercuric cyanide, and guano, boiled in linseed oil.

Copper and brass are recognised as the best protective agents for ships' bottoms against the influence of sea water, and marine animal and vegetable parasites, being used wherever possible. The employment of sheathing is, however, impossible on iron vessels, especially armour-clad ships, and is moreover too expensive for general use. Owing to the immense importance of the subject extensive investigations have been made by parties interested in the matter, with a view to discover an effectual means of preventing rust on the one hand and incrustations on the other, by coating the metal with some protective material that will be durable under all conditions, but no thoroughly reliable results have as yet been obtained.

Trials have been made in France in the employment of powdered copper, but with unsatisfactory results, because the preparation of the powder by galvanic methods proved too costly for technical purposes on the large scale, and the varnish selected as vehicle had not sufficient stability. All coatings for protecting iron vessels require very durable varnishes in conjunction with copper powder; otherwise—as reported by Wall—they will never effect their object. According to Wall's invention, copper powder may be produced very cheaply in such a condition that it can be incorporated

with suitable varnish and used like paint, the resulting coating affording equal protection to that of a sheathing of sheet copper. The copper powder may also be used in admixture with other pigments, *e.g.*, red ochre, lead peroxide, zinc grey, magnesia, bole, or ochre. As the edges of the iron plates cannot be so thickly coated with the paint as the plane surface, and are consequently more liable to rust under the influence of sea water, Wall employs a special method of priming which is claimed to preserve the metal from corrosion. The copper powder can also be made up into a paint with tar, or applied over a coating in which tar is present, or over a coat of red lead paint. It is well known that sheet zinc, or galvanised iron, affords an excellent protection against rust, though not against the corrosive action of sea water or incrustation by marine animals. No galvanic action takes place between the copper and iron in presence of sea water, for the reason that the copper powder is completely enveloped in varnish; consequently the destructive action of the sea water is prevented. If such action were possible, the copper would be soon converted into copper chloride, the rate of alteration being accelerated in direct proportion to the fineness of division. In any case this paint, like red lead, would require renewing after a while; but even porcelain or glass plates would be subject to slow corrosion.

According to a report of the U.S. Naval Institute, experiments have been made in coating the iron hulls of ships with Japan lacquer, the method being based on the observation that lacquered goods have been found to stand the influence of sea water for a considerable time. The Japanese Government purchased foreign-built iron and steel vessels, and, in view of the difficulties besetting the protection of ships' bottoms, experimented with lacquer. In the first place lacquered plates were immersed in sea water for a considerable time, and the results, though affording but little satis-

faction, were thought to be of sufficient interest to warrant further trials, particularly in the direction of rendering the lacquer composition more suitable for the purpose by means of various additions. In June, 1886, the first direct test was made by coating some 1,200 square feet of the keel of the warship *Fuso-Kan* with the lacquer composition hitherto found to be the best. In September, 1887, the vessel was dry-docked, when the lacquered plates proved, on examination, to be in such excellent condition that the Admiralty ordered the entire keel to be similarly treated. When the vessel was again examined in dry dock about twelve months later (December, 1888), the lacquer was found to be still intact and in no need of repair, the same proved to be the case in June, 1889, and April, 1890; nevertheless, for some unexplained reason the lacquer was then scraped off and replaced by a coat of paint. However, another series of experiments was subsequently made with lacquer on other Japanese ships, and Holte, the manufacturer of the composition, very soon held the monopoly of this method of employing lacquer.

The coating employed by Holte consists of pure lacquer, containing an admixture of mica or kaolin, *i.e.*, a perfectly inert material, the object of which is to give the lacquer more body and increase its binding power. The various successive coatings differ in that the earlier ones contain the largest proportion of pure lacquer.

Some time ago a patent was taken out for coating ships' bottoms with metal by electrolytic deposition. The inventor, D. W. Crane, has already completed the first practical experiment with this epoch-making discovery, and a short time ago coated one of the large ocean liners with copper by this means. The metal sides of the vessel serve as the negative pole, whilst the deposited film of copper forms the positive pole. The inventor proceeds by placing the electrolytic solution in troughs, which are wedged up (or attached by magnets)

against the hull of the ship and made watertight by caoutchouc joints. The current conveyed through the troughs causes the deposition of a layer of copper of the desired thickness on the sides of the vessel. The number of troughs employed naturally varies according to the area of surface to be coated. The individual sections of the precipitated copper unite to form a uniform jointless coating, making one piece with the ship's bottom.

According to Holzapfel, no favourable result as regards the preservation of the ship's bottom can be hoped for unless all loose paint belonging to a previous coating is removed; each speck of rust present must be carefully cleaned off, and then only should the surface be primed and painted afresh. If talc, red lead, or other paint has recently been applied to the ship's bottom, then only a very thin layer of certain compositions can be laid on, since otherwise the first paint will be dissolved by the vehicle of the second. Many compositions unite very well with old zinc white to form a hard, compact covering, which gives very satisfactory results. Zinc white is, moreover, the only ordinary paint that will adhere on new ships, though white lead is employed, particularly in dockyards, and is worthy of consideration where not excluded on account of expense. The white lead ensheathing the vessel is attacked by constituents present in the sea water, the resulting salts proving fatal to adherent animals. The first coating of composition applied to ships during, or shortly after, building never behaves very well, the coating becoming loose and gradually peeling off, carrying with it the superimposed layers of paint. This is to some extent inevitable, owing to the iron having begun to rust while the ship was in course of construction; partly, however, it is the result of the different paints used.

Tar paint, when fresh, is anti-putrefactive in action, but necessitates priming with some good composition.

The comparatively large number of anti-fouling compositions in current use may be divided into two classes: the first comprising such as partly prevent the adherence of testacea, and partly kill these organisms by the active poisonous constituents present; whilst to the second belong those covered by a superimposed layer of paint, which peels off, and by so doing ensures the removal of the incrusting testacea. The property of peeling off is often possessed also by the poisonous paints



FIG. 59 (natural size).—Non-peeling anti-fouling composition after three months' immersion in water.

With regard to these compositions, the following observations are made by Holzapfel: The best paints are the poisonous enamels, which, in addition to possessing toxic properties, are quick drying, adhere with a smooth surface, and do not peel off. To prevent peeling the mass must be applied to the object in layers, each of which is allowed to dry uniformly, in order to avoid inequality due to dissimilar vehicles. Copper salts, especially sulphates or oxides, form new combinations with the surrounding water, and are

gradually eaten away, *i.e.*, peel off. There are other materials which also possess dehiscent properties. Holzapfel, a manufacturer of a widely used composition, lays stress on the rendering of the preparation suitable to the portion of the ocean the vessel has to traverse, since the same formula is not adapted to serve in all waters.

The harder the paint the longer is it likely to last. Paints endowed with this property are therefore particularly suitable



FIG. 60 (magnified).—Non-peeling anti-fouling composition after three months' immersion in water.

for the Atlantic passage, whilst the more dehiscent (peeling) enamels are better adapted for the impure waters of the Indian Seas. In the former case a much smaller quantity of poisonous material is required, and renewal is less frequently necessary than in the latter waters.

On the question of paints for iron vessels, P. Schwarz says: "The object of the paint is to preserve the ship's bottom from corrosion or incrustation, and to colour the vessel above the water line. In the case of warships this colour should be inconspicuous, and for vessels in tropical

waters should be such as will exert a favourable influence on the internal temperature of the ship. In steel or iron vessels the principal point is preservation from rust, oxygen being present in large proportion in the air and the water, whilst the carbon dioxide of the bilge water has also a destructive action.

“Moreover, the scale (proto-peroxide of iron) produced in rolling the steel and iron plates, and the varying degrees of hardness of the surface developed during the working of the

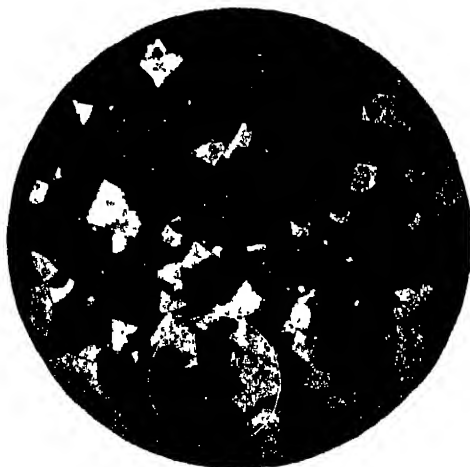


FIG. 61 (natural size).—Peeling anti-fouling composition after six months' immersion in water.

plates, give rise—in presence of sea water—to a galvanic current which leaves deep pittings of rust behind. Rust itself also forms a galvanic couple with iron in presence of sea water, decomposing the former, which then yields up its oxygen to further oxidise the iron, whilst the liberated hydrogen presses up the paint and contributes to its destruction.

“Consequently the preservation of the hull, and especially the protection of the bottom from corrosion by rust, is attended with great difficulties; and although a number of

compositions have made their appearance there is none that fulfils all requirements. Such paints must be insoluble in water, and sufficiently elastic to yield a little, thus preventing cracking, but at the same time should possess a certain degree of hardness to oppose sufficient resistance to mechanical shocks. These conditions are best fulfilled by a thin layer of resin; consequently many ships' paints are compounded of varnish to which metallic oxides in the state of powder are added in order to increase the oxidation and resinification of



FIG. 62 (magnified).—Peeling anti-fouling composition after six months' immersion in water.

the oil (this is, however, an erroneous assumption). Such materials include red lead, iron oxide, zinc white, and white lead, the resulting paints taking a long time—one to three days—to dry. More extensively used are the spirit varnish paints consisting of volatile oils or light hydrocarbon compounds and dissolved resin, which latter forms a thin, elastic, lacquer-like film on the surface of the iron after the solvent has evaporated. To this class belong the compositions made by Rathjen, Heyl, Dr. Pflug, Von Höveling, and many others, which are widely used in the mercantile marine service.



As they dry quickly, almost under the brush, the operation of painting requires but little time.

“Coal tar, which contains solid and liquid hydrocarbons and other matters, has also been found to behave well for ships’ use when prepared as free from acid as possible, though it wears away under the influence of sea water somewhat quicker than the previously mentioned paints

“Moravia composition, which is laid on either boiling hot or by means of a spatula, also behaves well in sea water, but owing to the inconvenient method of application has made very little headway.

“The destructive action of iron scale, already referred to, is obviated in the case of warships by pickling the steel plates. To this end the plates of the external skin are immersed for half an hour in a bath containing 17 to 18 per cent. of hydrochloric acid, after which they are scrubbed bright with steel brushes, and freed from any residual acid by steeping for a short time in lime water, followed by a final washing with warm water. After this they are generally coated with a thin layer of varnish to protect them while the ship is being built. Corrosion set up in the interior of the ship, by dirty bilge water, chemical action of cargo, or high temperature in the engine room and stockhole, is also usually guarded against by coats of paint—red lead and silicate paint. In the bilge, paint and cement and marine glue stopping are used, whilst special named paints—Crease’s paint—are employed in the water tanks. Cement being heavy is often mixed with coke, marine glue, etc.; and where carbon dioxide occurs in the bilge, slaked lime is often used to fix the acid.

“At the present time zinc is the best material known for protecting steel and iron against rust from sea water. Owing, however, to the expense of the treatment only the outer plates of torpedo boats, river boats and pontoons are galvanised, the thin plates of which ( $\frac{1}{8}$  to  $\frac{1}{4}$  of an inch thick) are liable

to become corroded right through. In large ships also, galvanised iron and steel are used for fittings exposed to air and moisture, which are consequently liable to be spoilt by rust; but since galvanising tends to weaken the metal it is now falling into disuse for important articles such as chains, cables, cleats, etc.

"In addition to the corrosion of iron on shipboard by rust, there also arise injuries due to galvanic action. Such occur at the stern when bronze propellers are used, and in bronze valves; in such cases it is usual to employ zinc protectors. Inside the ship no copper pipes should be led into the hold, consequently the lower lengths of the piping from the pumps are made of galvanised iron.

"Besides anti-corrosive paints, special value attaches to compositions intended to protect ships' bottoms from incrustation by vegetable (algae) and animal (mussels, crustacea) organisms, which in tropical seas especially accumulate to such an extent that the increase in surface friction may reduce the speed of the vessel by as much as one half. To remove this inconvenience, which greatly affects vessels both of the navy and of the merchant service, special paints are employed, or else the ship's bottom is covered with a metal sheathing, copper being the most efficacious. This metal oxidises uniformly in presence of sea water, the resulting copper compounds being so loosely adherent to the metal that they are washed away during the passage of the ship through the water, carrying any incrustation away with them. When the ship is at rest this action is more gradual; the copper may then become incrustated in course of time, or a galvanic action may take place between the copper and the iron. Consequently great care is necessary to insulate the iron plates of the vessel from the sheathing, in the case of sheathed iron ships. For the same reason iron bolts must be dispensed with in fastening metal sheathing on wooden

vessels, their place being taken by bolts of copper or yellow metal. The ship is then said to be copper fastened."

With reference to the composition of the various paints, Hummel says.—

"For priming, MacInnes used spirit varnish containing iron oxide, this being covered by a heated mixture of copper and soap. Gisborne mixed mercury and chalk and prepared therefrom a thick, slow-drying oil paint, which was then employed over a layer of red-lead paint. Rathjen's introduction of shellac dissolved in spirit must be regarded as an important advance in the protection of ships' bottoms. This solution was mixed with iron oxide, a little linseed oil being added in order to impart elasticity to the paint. This preparation served as a primary insulating layer and was covered by a second coating of the same materials together with arsenic and mercury. Such paints are characterised by great durability owing to the comparative impotence of the salt in sea water towards shellac, whilst the mercury in the upper coating becomes converted into mercuric chloride, which is fatal to the life of organisms. Rathjen's paints being quick drying it is therefore possible to apply two or three coats in the course of one day. It is, however, impossible to introduce large quantities of mercury into the paint, owing to its destructive action on the shellac; the latter is moreover only slightly soluble, so that the efficiency of the paint is greatly diminished. As poisonous constituents, mention may also be made of copper and zinc white, and other antiseptic materials, such as hydrazine, have been tried; the most efficacious, however, are copper and mercury. The cheapness of copper is in its favour, but nevertheless it cannot be regarded as perfect, because in case of injury to the insulating layer large quantities of copper are likely to effect the corrosion of the iron.

"The action of anti-fouling compositions manifests itself

either by their peeling off on the voyage and thus loosening the adherent incrustation, or else by the fatal influence of their poisonous constituents—salts of copper, arsenic or mercury—on the life of the incrusting organisms, which are thereby caused to fall away. Paints of the latter kind have, however, the disadvantage that the contained salts destroy the anti-corrosive primary paint and strongly attack the metal bottom. Moreover, it has not yet been definitely ascertained whether the poisonous salts actually remove the incrustation by killing the organisms."

For this reason preference is accorded to the peeling compositions. In such cases the protecting paint must be renewed annually, which renders it unsuitable for ships that have to make long voyages in tropical waters. For the latter, metallic sheathing affords the best protection against incrustation. As regards colour, ships voyaging in the tropics are always painted white above the water line; ships of war receive a covering of grey to dirty yellow paint, though latterly olive green has been found more suitable on account of its rendering the vessels practically undetectable at distances whereas they can be plainly seen when painted in other colours. Torpedo boats and despatch boats are generally painted black, whilst the painting of merchant vessels and yachts is altogether a matter of taste.

Hummel lays down the following fundamental conditions for the suitability of paints for iron ships:—

1. The composition must preserve the ship's bottom from corrosion;
2. It must form a smooth surface, in order to diminish friction; and
3. Must dry quickly, so as to enable the parts below the water line to be cleaned and coated with two coats of paint in a day.

In the case of new steel vessels the plates are generally covered with a skin, which must be removed by dipping in

dilute hydrochloric acid; otherwise this layer peels off, carrying the paint with it, thus exposing the naked metal to corrosion. New ships should also be painted at least once every six months until it is certain that the paint has obtained a firm hold.

In order to show the relative value of the existing anti-fouling compositions, the subjoined table has been compiled by W. P. Wierchowski, on the basis of experiments made with the Baltic fleet:—

Composition.	Consumption per	Cost.	Weight of
	square fathom of surface.		incrustation per month.
	Lb.	Roubles.	Lb.
Leoni Nos. 1 and 2	7.00	2.55½	3.704
Rathjon Nos. 1, 2, 3	6.18	4.95	3.191
Dubois Nos. 1 and 2	7.50	3.72	5.453
Perret Nos. 1 and 2	7.86	2.90	4.858
Holzappel Nos. 1 and 2	7.25	2.70	3.168
Murres Nos. 1 and 2	9.03	5.12	3.775
Soapstone	5.25	0.79	5.455
Urban No. 1	6.00	1.80	2.82
Urban No. 2	10.50	5.77	2.82
Red Lead	6.50	0.70	8.02

### VARIOUS SHIP PAINTS.

#### *Gisborne's Paint.*

Consists of—

Mercury	5 parts.
Chalk	7½ "
Lead oxide	4½ "
Zinc white	7 "

(or white lead and red lead) incorporated with linseed varnish by grinding.

#### *Lucchini's Anti-corrosive Composition.*

Gallipot	30 parts	} dissolved in
Pure resin	20 "	
Mineral oil	30 "	and
Turpentine	15 "	mixed with
Manganese dioxide	6 "	and ground along with
Mercury arseniate	2½ "	and
Red arsenic	20 "	
	15	

*Carr and Dickinson's Paint.*

Resin . . .	100 parts, dissolved in
Carbon bi-sulphide . . .	91 „ and
Naphtha . . .	18 „ the filtered solution being mixed with
Pigment . . .	19 „ and a little powdered lime.

*John Haddon's Paints for Ships' Bottoms.*

This inventor patented the following composition :-

Iodine . . . . .	1 part, dissolved in
Alcohol . . . . .	1 „ and mixed with
Vegetable or mineral carbon . . .	20 parts,
Carbolic acid . . . . .	2 parts, and
Iron oxide . . . . .	76 „

the whole being ground along with a suitable proportion of linseed varnish.

*Cheap Paint for Iron Ships.*

Asphalt, or black pitch . . .	600 parts, melted and mixed with
Hot boiled linseed oil . . .	480 „ the whole cooled to 24° C., and mixed with
Graphite . . . . .	600 „
Copper arseniate . . . . .	120 „ and
Coal-tar oil . . . . .	640 „

The intimately incorporated material is applied hot to the ship's hull.

*Kitchingham and Andrews' Paint.*

Hot tar . . . . .	2½ parts
Iron oxide . . . . .	2 „
Resin . . . . .	1 part
Lead acetate . . . . .	2 parts

mixed together and applied whilst hot.

*Schnittger's Paint for Ships' Bottoms.*

In compounding this paint, the inventor (Schnittger, of Cologne) was careful to ensure its peeling off- and at the same time exerting a poisonous effect--as soon as infested with any considerable incrustation. The method of preparation is as follows: 10 parts of copal are distilled with continuous stirring until 20 per cent. or so has been vapor-

ised, the vapours being collected and condensed in a separate vessel. The remaining 80 per cent. of the copal is then run out of the still and rapidly cooled, by pouring into cold water; the mass is then broken up, and dissolved in 90 per cent spirit on the sand bath, the temperature being kept as low as possible. This copal varnish is filtered, mixed with the distilled copal oil, and reduced with spirit; the aqueous distillate must not be added, as it would cause precipitation.

The following alcoholic solutions are next prepared :—

2	parts of powdered aloes	in	4	parts of 90 per cent. spirit
2	„ camphor	„	4	„ „
2	„ pitch	„	4	„ „
5	„ colophony	„	3	„ „

these being added to the first one in a large vessel, left to clarify, and afterwards decanted from the sediment. Of this carefully prepared solution 33 parts are mixed, by continual stirring, with 28 parts of *Caput mortuum*, 3 parts of linseed oil, and 3 parts of castor (ricinus) oil. After prolonged stirring, 10 parts of *hydrargyrum oxydatum rubrum s. flavum* are stirred in, followed by 5 parts of crystallised carbolic acid, the whole being then stirred for a further twelve to twenty-four hours, and packed in casks.

#### *H. and F. G. Benedikt's Paint for Ships.*

Hydrated protoxide of copper is precipitated by reducing copper sulphate with grape sugar and potash, the precipitate being mixed with carbolic acid, then warmed and incorporated with linseed oil followed by some mineral pigment. The cuprous carbolate presumably formed is claimed to permanently exert a particularly poisonous effect on animal and vegetable matters.

#### *Satin's "Incomparable" Waterproof Varnish.*

Louis Satin prepares the following composition for pre-

venting access of water, rusting, or incrustation by crustacea and plants :—

For the first coating 40 parts of water-free tar are heated and mixed with 40 parts of coal tar and 60 parts of tar oil. This mixture replaces the usual red-lead and linseed-oil paint. The second coat—for killing the incrustation—is made of 35 parts of oil-free tar, 20 parts of coal tar, and 40 parts of tar oil, 40 parts of some poison—such as arsenic, corrosive sublimate, mercury arsenate, Schweinfurt green, etc.—being added per 100 parts of the mixture.

*Harrison's Composition.*

	Parts	Parts
Trinidad pitch . . . . .	35	heated and mixed with slaked lime 45
Finely ground barium carbonate . . . . .	25	and powdered copper sulphate . 5

When mixing is completed and the mass has cooled down to 100° Fahr., a suitable proportion of crude naphtha or turpentine is stirred in.

*Cook's Composition.*

Shellac . . . . .	2 parts,
Grain lac . . . . .	$\frac{1}{2}$ part,
Gamboge . . . . .	$\frac{1}{2}$ „
Benzol . . . . .	$\frac{1}{2}$ „ and
Red lead . . . . .	1 „ are dissolved in
Alcohol . . . . .	8 parts.

The clear solution is used for the first coat; for the second coat it is mixed with—

Zinc white . . . . .	1 $\frac{1}{2}$ part, and
Verdigris (copper acetate) . . . . .	$\frac{1}{2}$ part.

*Cruickshank's Composition.*

A solution of resin is prepared, at the rate of 10 lb. per  $\frac{1}{2}$  gallon of turpentine, to each gallon of which is added  $\frac{1}{2}$  gallon of gutta-percha solution (4 lb. per gallon of turpentine). Each gallon of the mixture is incorporated with 5 $\frac{1}{2}$  lb.



of red mercury oxide, "white precipitate," or mercury oxychloride, and 5½ lb. of red lead.

*Submarine Paint for Ships, Quays, etc.*

Hydrated copper oxide is prepared by reducing copper sulphate with potash or starch sugar, the precipitate being incorporated with carbolic acid, and mixed in a moderately warm condition with linseed oil and any desired mineral pigment. The resulting paint is highly poisonous to all animal and vegetable organisms.

*J. M. Lintock's Paint for Ships' Sides.*

Twenty parts of zinc white and 6 parts of linseed oil are mixed and thoroughly incorporated by stirring with 14 parts of tallow, previously deprived of moisture by means of steam heat applied during several hours. When cooled the mass is reduced by agitation in a close air-tight vessel with 7½ parts of naphtha, benzol, or the like, 3 parts of gum dammar, and 1 part of colophony. After the preparation has cooled down, which takes about twenty-four hours, the zinc white will be found diffused in a finely divided state throughout the mass.

*O. L. Burnham's Paint for Ships' Bottoms.*

This is composed of seaweed ground, in a green and moist condition, in linseed oil, and mixed with oil, litharge, lead acetate, and turpentine. It is claimed that this paint, in addition to acting as a preventive against incrustation by mollusca, also protects wooden vessels from the ravages of worms below the water line. The method of preparation is the following: Linseed oil, about 10 gallons, is boiled for five hours at 600° Fahr., together with ½ lb. of litharge and ½ lb. of lead acetate, and then reduced to proper workable consistency with turpentine, a pint of seaweed—previously

ground in a freshly gathered state in linseed oil—being added, and the whole coloured by ochre or other suitable pigment.

#### VARIOUS ANTI-CORROSIVE PAINT MASSES.

Under this heading may be comprised all such compositions—paint masses, processes, and the like—as are used for painting the surface of metal, although they may not be true oil paints. The value of these preparations is a variable quantity, and there are several that would be very serviceable if resistance to atmospheric influences were not in question.

##### *Buechner's Anti-corrosive Preparation.*

In manufacturing this preparation the inventor (Dr. August Buechner, of Heidelberg) employs a mixture of metallic zinc and calcium carbonate in a very finely divided state, along with some polishing material, such as levigated Tripoli, colcothar, or vegetable charcoal, the whole of these constituents being thoroughly dried, sifted, and finally bolted. The mixture is then incorporated with an alcoholic solution of soap of specific gravity 0.925, prepared by mixing 2 parts of a soap made of olive oil, potash lye, alcohol, and water with 1 part of a soap made from olive oil, hog fat, lead oxide, potassium carbonate, and water. To the mixed soaps benzol is added until the limit of limpidity of the solution is just reached. The powder and liquid are stored separately, as, when mixed together, they cannot be kept in closed vessels owing to their mutual reaction. Shortly before use the components are intimately mixed in a basin by stirring with the brush afterwards used for painting, 1 part of powder being employed with 2 parts of the soap solution. After setting aside for ten to fifteen minutes in a cool place the mixed paint is ready for use. The ironwork to be painted must previously be carefully freed from grease and impurities. For articles kept under cover a single coating will suffice,

but two coats are applied to those exposed to the weather. The paint is laid on in such a manner that the sheen of the metal surface is no longer visible. The mass dries under the brush, and becomes so hard and fast after a few days' exposure to the air that it cannot be washed off by even the heaviest and most prolonged fall of snow or rain. When the articles are to be used the coating can be easily removed by brushing. Unlike the ordinary anti-corrosive paints, *no* resinification or greasing occurs in this preparation; the polish and lustre of the metal are also preserved for years, being even increased owing to the action of the polishing materials during the removal of the mass.

Iron and steel remain free from rust for so long as the surface is covered with the paste; the material is also suitable for preserving from rust weapons of all kinds, as well as fine surgical instruments, machinery at rest, extra machine parts and other articles kept in store.

To permanently protect iron structures from corrosion, for instance bridges, girders, and so forth, the above-mentioned powdered mixture—minus the polishing material—is incorporated with an alkaline solution of glutin, in place of the alcoholic soap solution. This is prepared by agitating a boiling aqueous solution of glutin with successive portions of a hot, concentrated mixture of sodium borate and potassium carbonate, the whole being then gently boiled for half an hour. After storing in a cool place for fourteen days in a well-closed vessel, and filtering through wood charcoal, a clear, non-glutinous liquid of specific gravity 1.0350 is obtained.

The method of application is the same as already described, the ratio of powder to glutin solution being in this case 2 : 1 by weight. The paint dries quickly, and, unlike the first preparation, sets so hard within a few hours that its removal by mechanical means is extremely difficult. Owing

to this property, the preparation is highly suitable as a priming coat for oil paints, the latter rendering the protective layer waterproof and therefore durable. The advantages of this material in comparison with the red-lead paints hitherto used are self-evident. The paint does not peel off like red lead often does, besides which the injurious action exerted by the metallic sulphides and sulphuric acid salts present—often in large proportion—in iron oxide paints is entirely obviated. Since a single coating is sufficient, the method recommends itself owing to the great saving of time it affords, apart from the low price of the preparation.

*Ebers' Anti-corrosive Paint.*

F. Ebers & Co., of Düsseldorf, employ linseed oil or some other drying oil or resin, heated along with 10 per cent. of free linolic acid (or other drying fatty acid) and copper oxide, copper benzoate, or a compound of copper with the fatty acid of a drying oil, until partial or entire solution has been effected. The liquid is then filtered and mixed with a drying oil in such proportion that the whole contains about 2 per cent. of copper and is still rich in the free (drying) fatty acid.

*Buechner's Process for Destroying and Preventing Rust.*

This method (which is protected under the "Useful Design" branch of the German Patent Law) relates to the preparation of a mixture of various substances for destroying rust immediately and preventing its recurrence—a danger always imminent when rust is removed by the aid of chlorides or acids, due to the presence of residual dilute acid, etc., on the surface of the metal after the latter has been washed. The fact that iron or steel freed from rust by treatment with such chlorides or acids soon becomes covered with a thicker layer of rust than ever has led to the

abandonment of this practice in favour of scrubbing with emery and other polishing materials, but this latter method has the disadvantage of injuring the unruined portions of the metal; moreover, the rust is sometimes inaccessible to emery on account of the shape of the article to be treated. These defects the inventor claims to have overcome by means of the following liquid, which immediately removes any pre-existing rust on iron and prevents further rusting—conditions essential to any anti-corrosive which has any claim to practical utility. The material employed consists of rosolic acid, sulphuric acid, tartaric acid, ferrous sulphate, potash alum and vegetable mucilage, prepared as follows:—

1. Five parts of gum tragacanth are thoroughly softened with 200 parts of water and then dissolved by heat on the water bath.

2. Three and a half parts of tartaric acid are dissolved in 50 parts of water and mixed by agitation with 0.5 part of chemically pure sulphuric acid, powdered rosolic acid being added to the warm liquid and left to dissolve.

3. The two liquids are mixed by pouring No. 2 into No. 1, stirring the whole time until a homogeneous mass is produced.

4. Finally a solution of 10 parts of pure ferrous sulphate and 5 parts of potash alum in 100 parts of water is added, the whole being shaken up in a flask and filtered through glass wool.

To remove rust from the surface of large objects the affected spots are painted over with the liquid, which is left to act for some time, and afterwards wiped off along with the rust by rubbing with a clean rag. Smaller articles which cannot be treated separately, *e.g.*, sewing needles, thimbles, knife blades, steel pens, bottle stoppers, steel cartridge cases, screw attachments to firearms, etc., are dipped in water containing some of the above-mentioned fluid, until all the rust has been removed. They are then

taken out of the bath, well drained and finally shaken up for a long time in a mixture of dry sawdust 6 parts, fine chalk 3 parts, and 1 part of finely powdered quicklime. The preparation does not attack either iron or steel, nor does it affect their polish.

*Dr. C. Levoir's Method of Preserving Iron from Rusting.*

The iron is warmed to about 40° C. over a coke fire (spirit or benzine lamps being unsuitable by reason of the water engendered during the combustion of these liquids depositing on the metal) and then rubbed over with a rag previously soaked in linolic acid diluted with methyl alcohol containing a small percentage of dissolved rosin. The layer resulting from this operation, though not perfectly hard, greatly facilitates the adhesion of paint on iron, and prevents the rusting of the metal by itself absorbing oxygen continuously. At the end of twenty-four hours a second coating is applied, consisting of a workable paint of equal parts of red lead and white lead ground in boiled oil and containing up to 10 per cent. of linolenic acid. According to the inventor this mixture of white lead and red lead adheres more firmly and is more durable than red lead alone. It should be laid on sparingly, and will dry in three hours; an interval of twenty-four hours is, however, desirable before applying the next coat.

Levoir claims that, treated in this manner, iron will withstand both the influence of weather and of salt spray, whereas red-lead paint used alone is attacked by sea water to such an extent that, at the end of three years, no trace of lead can be detected in the scrapings of the paint.

There are no practical objections against this process, and a test on a large scale is not difficult to make.

For the preparation of linolenic acid on a manufacturing scale Levoir gives the following instructions:—

Old clear linseed oil is stirred up with 15 per cent. of slaked lime and boiled with plenty of water, the operation

being accelerated by employing a pressure of  $2\frac{1}{2}$  atmos. The resulting lime soap is then mixed, by heat and agitation, with 130 parts of 33 per cent. sulphuric acid in a lead-lined vessel, the linolenic acid, which gradually collects on the surface, being drawn off and washed with water to remove any residual sulphuric acid.

### *Linolic Acid.*

To prepare linolic acid, linseed oil or poppy oil is completely saponified with caustic soda lye, the soap being purified by treatment with hot water and soda lye, followed by repeated salting out. The soap is then dissolved in a large volume of water, and decomposed with calcium chloride, the lime salt of the fatty acids being thrown down. On washing and pressing the precipitate and treating it with ether the calcium linolate is brought into solution, leaving the lime salts of the other fatty acids undissolved. The ethereal solution is next decomposed with dilute hydrochloric acid, whereupon the calcium chloride formed dissolves in the water present, whilst the linolic acid remains in solution in the ether. The solvent can be distilled off at a low temperature, in an atmosphere of hydrogen, after separating the two layers of liquid. The impure linolic acid left in the still is dissolved in alcohol and thrown down by ammonia and barium chloride as barium linolate, which is washed, pressed, treated with ether, and recrystallised several times. To obtain the linolic acid the barium salt is shaken up with ether and dilute hydrochloric acid, the ethereal layer being then drawn off and distilled as before, the residual acid is then dried under the air-pump, in presence of sulphuric acid and a mixture of lime and ferrous sulphate (for the purpose of absorbing oxygen). A nearly pure linolic acid can also be prepared by decomposing lead linolate with sulphuretted hydrogen and extracting with ether.

Linolic acid—Mulder's "linolein"—is a thin, pale yellow oil, of specific gravity 0.9216, at 15° C., with a high coefficient of refraction and faintly acid reaction, mild flavour at first, but leaving an irritating after-taste in the throat. It does not solidify even at -18° C., is insoluble in water, but dissolves readily in alcohol and ether. When exposed to the air, linolic acid absorbs oxygen (about 2 per cent.) with avidity, becoming thick and viscous, changing finally into a mass resembling varnish. Spread out in thin layers on wood it forms a varnish, but on glass it merely thickens. By treatment with hydriodic acid and amorphous phosphorus linolic acid is converted, by the nascent hydrogen, into stearic acid. In an undecomposed state it is non-volatile, and the products obtained by distillation are different from those furnished by oleic acid. It does not yield sebacic acid. Nitrous acid and hyponitrous acid render linolic acid viscous, without any deposition of elaidic acid crystals or other allied acid occurring. Nitric acid causes it to swell up considerably and change into a greasy resin. Owing to their instability and tendency to form acid salts, the linolates are difficult to obtain in a pure state. They are white in colour, usually non-crystalline, and separate out in flakes as the hot-prepared alcoholic or ethereal solution cools; when left to evaporate spontaneously a gelatinous residue is formed. The salts turn brown on exposure to the air, and develop a characteristic aroma. According to Hazura, linolic acid is not a pure substance, that from *linseed oil* consisting of—

Linolenic acid	.	.	.	.	.	15 per cent.
Isolinolenic acid	.	.	.	.	.	65 "
Linolic acid	.	.	.	.	.	5 "
Oleic acid	.	.	.	.	.	15 "

while that from *poppy oil* is composed of—

Linolenic acid	.	.	.	.	.	5 per cent.
Linolic acid	.	.	.	.	.	60 "
Oleic acid	.	.	.	.	.	85 "



In their observations on the phenomenon of drying, Hazura and Bauer found that these drying acids behave similarly towards atmospheric oxygen, except that the time required for oxidation is different; linolenic acid and isolinolenic acid being the quickest drying.

*Rubber Oil (Anti-corrosive).*

According to the Patent Specification, this preservative is prepared by redistilling the crude oils obtained from the dry distillation of brown coal, peat, or other mineral resinous substances. Thin rolled india-rubber is cut into fine strips and soaked in four times its own weight of the resulting oil during a period of eight days, the product being then exposed to the action of vulcan oil or a similar body until a perfectly homogeneous clear mass is formed. When spread very thinly over a metallic surface and left to dry slowly this substance forms a kind of skin capable of effectually resisting atmospheric influences.

*Jokl and Randnitz's Method of Protecting Iron and Steel from Rusting.*

A permanent layer of oxide is formed on the surface of the metal by dissolving 1 part of zinc oxide, lead oxide or alumina, or the corresponding chlorides, in 3 parts of some mineral acid—such as sulphuric, nitric, or hydrochloric acid—diluting the solution with 100 parts of water containing 1 or 2 per cent. of tartaric acid, citric acid, potassium-sodium tartrate, or sodium nitrate, etc., and utilising the finished liquid for dipping the iron articles to be treated. After two to ten hours' immersion the iron is dried at 100° C. in an oven until the superficial moisture is dissipated, after which it is dipped in a liquid hydrocarbon (*e.g.*, petroleum residue) and exposed over a coke fire, or to air heated to the temperature

of combustion of the hydrocarbon. The finished surface can be rubbed over with a mixture of graphite and paraffin.

*Benenont's Anti-corrosive Insulating Paint.*

A resinous substance is dissolved in carbon bi-sulphide, a suitable mineral salt, insoluble in water, being added to the solution at the proper moment, a silicate being preferable for this purpose. The general proportions are: Carbon bi-sulphide, 100 parts; resin, 45 parts; and 45 parts of silicate or other coloured or colourless salt. The finished product may be colourless or coloured, dries at once owing to the rapid volatilisation of the solvent, leaving a waterproof, insulating layer protecting the metal against oxidation, and being, in addition, fireproof and impervious to the action of acids and alkalis. The paint forms a lustrous, unalterable coating, which, on account of its impenetrability by moisture, can be used in place of glazed bricks or cement in building operations or for decorative purposes, being of the same colour as these materials, and much cheaper. The excellent qualities of the paint are completely developed within a few days after application.

*B. Pollitzer's Protective Surface for Metallic Objects.*

The bright or oxidised metal surface to be protected is suitably prepared by smoothing, and afterwards coated over with a thin layer of one or more drying oils, such as linseed oil, Bankul nut oil, nut oil, hemp oil, poppy oil, castor oil, cucumber seed oil, sunflower oil, pine seed oil, cotton seed oil, grape seed oil, etc., either by dipping, by painting with a brush or other suitable means, according to the metallic object to be treated. The article is then exposed, in a suitable apparatus, to a temperature of 200° to 400° for half to one hour, which treatment causes the oil to form a hard, lustrous, elastic, and firmly adherent mass.

*Cosmann's Anti-corrosive Paint.*

Dr. Cosmann (Ger. Pat 93,854) employs the peroxides of the noble metals cerium, didymium and lanthanum, which act on linseed oil like the heavy metals. These orange-red to straw-yellow coloured oxides are of lower specific gravity than the heavy metals; they are therefore more economical weight for weight, easy to prepare, and are obtained as by-products from monazite sand. Since when ground up with varnish, they form paints of good covering power, it seemed feasible to impart to these paints both drying properties and a lacquer-like character by heating them to 150° C., for some time. By this means an exceedingly good covering paint, which is quick drying and extremely durable, is obtained; it is suitable for painting iron, requires no priming, and forms neither wrinkles nor cracks. These earths are absolutely neutral bodies which, unlike metallic oxides (micaceous iron ore, zinc dust, etc.), exert no galvanic action on the iron; moreover, they are able to resist even strong acid fumes, and consequently are endowed with all the properties required of an anti-corrosive material.

*Leando Borgnini's Method for Coating Sheet Metal with an Acid- and Alcohol-resisting Layer.*

An excellent medium for coating or painting sheet iron, especially the walls of vessels used for the conveyance of wine and other liquids, is afforded by shellac, this substance protecting the metallic surface against the action of the acids and alcohol present in small proportions (less than 25 per cent.) in the said liquids.

The hot method of lacquering with shellac is performed in the following manner: The sheet metal must first be thoroughly cleaned and treated with dilute sulphuric acid, whereupon the application of the shellac is proceeded with, on a small section of the surface at a time. With this object

the part to be lacquered is heated, and when the requisite temperature is obtained the shellac (in sheets or scales, as met with in commerce) is placed on the heated surface, where it melts and can be distributed by means of a brush or other suitable means until the layer is of the desired thickness. On cooling the metal the lacquer will be found hard and solid.

The crux of the operation is the determination of the proper degree of heat to be applied to the metal, since, if insufficiently high, the lacquer, though melted, will not adhere but breaks away under the slightest shock, whilst if the heat is too great the shellac is to some extent burned, or at least becomes spongy and therefore useless.

As soon as one part of the metal has been covered another portion is treated in the same manner, and the operation continued until the whole surface is lacquered over. The layer should be about  $\frac{1}{8}$  of an inch in thickness.

Shellac can also be applied by the brush in the form of an alcoholic solution, as it dissolves very readily in this liquid. To prepare such a varnish the shellac is converted into coarse powder which is placed in an excess of alcohol, so that the undissolved residue is small in amount. The mixture is boiled and stirred for about a quarter of an hour to complete the solution, and is decanted after two hours' repose.

This varnish is brushed over the previously well-cleaned metal surface and thoroughly dried by exposing the sheet in a room warmed to 30° to 40° C. A second layer is applied in the same way, and so forth, care being necessary that each one may dry properly before applying the succeeding coat. Eight or ten applications are needed to produce a layer of sufficient thickness to be resistant. An addition of 5 per cent. of hydraulic cement can be made to varnishes of this kind, no difference being made in the mode of application.

The sheet metal may also be coated with a layer of hydraulic cement before the varnish is laid on, with which object a little cement moistened with an agglutinant liquid may be brushed over the cleaned surface of the metal, so as to produce a thin continuous film. After this film is dry a second layer of cement is applied in the same manner as to the surface of a wall. Then, when the cement adheres and has become quite dry at the ordinary temperature, the surface is washed over with a 20 per cent. solution of tartaric acid, left to dry thoroughly, and topped with a 4 per cent. alcoholic solution of shellac, laid on warm (about 50° C.) with the brush. Instead of this varnish the cemented surface may be covered over with a layer of 36° Bé. water glass (sodium silicate), applied in five or six separate coatings, the surface being washed over with hot water when dry. Alternatively the cement may be brushed over with melted paraffin (temp. 150° to 200° C.) in sufficient quantity to impregnate the mass, the surface being finally washed carefully with hot water.

*Rieglmann's Anti-corrosive Paint.*

Ordinary linseed oil paint is mixed with 10 per cent. of calcined magnesia, baryta or strontia, and mineral oil. This is claimed to neutralise the free acid of the paint and, in consequence of the alkaline reaction, preserve the iron from rusting. To keep iron free from rust when embedded in the earth the metal is coated with a mixture of—

Pine resin	.		100 parts.
Gutta-percha	.	.	25 "
Paraffin	.	.	50 "
Magnesia	.	.	20 " and
Mineral oil.			

For use on machine parts the paint containing 20 to 30 per cent. of magnesia or calcined dolomite is mixed with vaseline to keep it from drying.

*Unalterable Paint for Cast Iron.*

The articles are cleaned with weak acid, dried, and rubbed over with a file, wire brush, etc., to make them quite smooth. They are next rubbed several times with ordinary crude petroleum and allowed to dry after each application. A dark glossy appearance is then imparted by friction with a stiff brush made of bristles, which glossy surface remains unaffected even by the heat of a stove, and affords an efficient protection against rust. Having thus laid the foundation for a lustrous exterior, it will be sufficient to afterwards simply rub the surface over with petroleum and polish with the brush to form a progressively increasing gloss of dark shade on the surface of the cast iron.

*Gelder's Anti-corrosive Paint.*

A solution of sodium silicate (water glass) is added to one of zinc acetate, and the freshly precipitated zinc silicate is mixed, whilst still moist, with linseed oil and zinc white. According to Simon, the zinc silicate prepared in this manner is not free from water of hydration, and consequently the power of resisting the effects of weather and of affording protection against rust is imperilled. If, however, the product be gradually calcined, it will not sinter—if properly handled—but can be readily ground to a fine powder, then forming a pigment which meets all requirements.

*Anti-corrosive Weatherproof Paint Containing Paper.*

Starting with the idea that a simple wrapping in paper suffices to protect iron and steel from rust, Cross and Bevan patented a process for dissolving paper or cellulose, and thus converting it into a suitable form for incorporation in paint. Ammoniacal copper oxide being at once too dear and incapable of yielding satisfactory results, the inventors dissolve cellulose paper in 15 per cent. caustic soda lye, and treat the

product with carbon bi-sulphide for two to three hours, whereupon a yellow-brown mass is formed, known as cellulose xanthate or viscose. By dissolving 16 parts of this mass in 100 parts of water the paint is formed, and can be mixed with lampblack, red lead, colcothar, or other pigment as required, a drier, such as lead acetate, magnesium chloride, etc., being added just before use. This renders the paint hard, weatherproof, and perfectly unalterable; it adheres equally well on stone, wood, or metal, and does not peel off like lacquers and varnishes. It is stated that this preparation has proved very satisfactory as a paint for iron ships.

*Hydroferrocyanic Acid as an Anti-corrosive.*

The articles of iron or steel to be treated are painted over with a solution of hydroferröcyanic acid or hydroferricyanic acid in conjunction with a strong acid, this treatment resulting in the solution of a small proportion of the metal and the formation of a very good anti-corrosive layer of insoluble double salts on the surface. According to an improved modification of this method the aqueous solutions of the above-named acids may be replaced by their alcoholic-aqueous solutions with or without an addition of oil, the advantage being that these are better distributed over the metallic surface.

*Hohenberg's Paint for Metallic Articles.*

The cleaned surface of the articles—especially tins for conserves, pudding moulds, and aluminium flasks—is covered with one or more coatings of a mixture of permanent white (barytes or zinc sulphide white) and egg albumin, and when dry exposed to the action of boiling water or steam

*Plastique Bourdin.*

This is a paint intended to protect wood or iron from the action of acids. It is prepared by melting together powdered

wood charcoal and resin or colophony, with an addition of boiled linseed oil, vaseline, spermaceti and bone black, in varying proportions, which are determined by the colour, viscosity, and distributing power required, resin and wood charcoal are, however, prescribed as principal ingredients in all cases. For use, the mixture is melted, and is said to form a hard solid coating unaffected by acids

*Metal Paint from Spathic Iron Ore.*

D. Aichelburg, of Billach, Carylthia (Ger. Pat. 75,788), employs the native iron ore known as sphaerosiderite (ferrous carbonate) or white iron ore, which by careful grinding and levigation is converted into "Montanite" paint for metal. The preparation, however, has a lower covering power than other iron oxides, though it is much dearer than the latter.

*Silver Slag as an Anti-corrosive Paint.*

Silver slag, having a high percentage of silica and containing lead and zinc in the form of silicates, is capable of absorbing considerable quantities of varnish, and is perfectly indifferent towards chemical reagents. It is stated that ten years' practical experience with paints containing at least 40 per cent. of this pigment has led to the conviction that their anti-corrosive and weather-resisting properties are superior to ordinary lead paints.

*Robson's Metal Paint*

consists of resin pitch, either alone or in conjunction with residue from the distillation of mineral oil or ozokerite—or with any other pitch that is miscible with paraffin—to which is added mineral oil or other oil. The object of the invention is to produce, without any admixture of drying oil or volatile solvent, a paint mass which will become fluid when heated, is of low viscosity, and possesses just sufficient tackiness to



cause it to adhere to the metal, so that it can be distributed by the brush without difficulty

*Walter and Stone's Anti-corrosive Paint*

Tannic acid and some agglutinant substance (gum-arabic dextrin, etc.) are dissolved in water or glycerine and mixed. This mass when applied to iron or steel in the ordinary manner by the brush forms a durable and efficient coating for the most part insoluble in water and constituting a good substratum for other paint and lacquer

*Matthew's Caoutchouc-graphite Paint.*

The mass for this paint, which is intended for metal roofs, and wooden structures of all kinds that are exposed to water, is invented and patented by Matthews of Harrisburg (Pa.), and consists of a linseed oil solution of caoutchouc ground together with graphite to a thick but readily distributable mixture.

*Heald's Anti-corrosive Paint.*

Having repeatedly observed in the dismounting of gas-meters that, whilst the old iron plate was generally corroded, the inscriptions marked thereon for transit purposes remained entirely unaltered, John Heald, of California, formed the idea of trying a mixture of white lead and turpentine as a rust-preventing coating for iron, and found that by using finely ground white lead in suspension in turpentine spirit the metal neither rusted nor scaled on the parts covered with this preparation.

SUNDRY PAINTS FOR IRON.

1. Twenty-four parts, by weight, of asphalt are dissolved in a flask in 36 parts of benzol at a moderate heat over the sand or water-bath, and when this is complete the liquid is

left to settle in a warm place (15° to 19° C.), separated from the sediment by decantation, and mixed with a solution of 2 parts of hard elemi resin and 1 part of copaiba balsam in benzol, the whole being reduced to the proper consistency by an addition of the same solvent.

No objection can be raised against the usefulness of this preparation ("iron lacquer"), but the employment of copaiba balsam makes it too expensive for use on a large scale.

2. Fifty parts of poppy oil are well boiled, and at once added to a mixture of equal parts of litharge and manganese hydrate, the whole being well stirred, incorporated with 25 parts of benzine, and left at rest for twenty-four hours.

It may be stated that linseed varnish and benzine would produce the same result at less expense.

3. A 10 per cent. solution of flowers of sulphur in turpentine is prepared and mixed with half the quantity of linseed varnish, added by instalments. A quantity of graphite equal to the weight of sulphur used is then stirred in along with an amount of dissolved asphalt equivalent to the linseed oil. The preparation should be slightly warmed before use.

4. Ten parts of water-free tar, deprived of every trace of acetic acid—or ammonia and its compounds if coal tar be used—are boiled and mixed with 2 parts of graphite and 1 part of red lead. After the whole has been well boiled together, 1 part of flowers of sulphur and 2 parts of calcined pumice powder are thoroughly mixed in by stirring.

This is about equal to any good tar paint

5. Equal parts of verdigris and white lead are stirred up with 3 parts of linseed oil until a thick pulp is formed, whereupon 1 part of hot turpentine, 1 part of zinc dust, and 1 part of chalk are stirred in.

This is a linseed oil paint devoid of any special advantage over others of this class.

6. Twenty-six parts of paraffin are dissolved in 80 parts of crude petroleum, and added to a mixture of 40 parts of linseed oil, 20 parts of flowers of sulphur, and 36 parts of pine resin.

The paraffin-benzine solution renders the coating soft and unstable, but it is useful for certain purposes.

7. Equal parts of a 50° Bé. solution of water glass and finely powdered zinc white are well mixed and stirred so as to produce an easy working paint.

Zinc white will not mix with water glass without coagulating and forming an unworkable mass.

8. The articles to be treated are placed on a grating in an iron cylinder, the bottom of which contains small coals. On closing the cylinder and raising the lower end to red heat, the articles become covered with a shiny coating of magnetic oxide which decreases in lustre the longer they are left in the cylinder.

This method is highly suitable for small articles.

#### VARIOUS MEANS FOR PREVENTING RUST.

##### *Fats, Oils and Compositions prepared therefrom.*

It has already been mentioned in a previous section that fats and oils afford good protection from rust in cases where such protection is only required to be of a temporary character and no exposure to the action of the weather is in question. The function of these fats and oils consists in forming an impervious, rust-preventing layer on the iron, which being easily damaged by mechanical influences, can be of value only for objects that are to be kept stored in closed rooms and not those which are to be used.

When prolonged storage is in question a selection must be made, among the fats and oils, of those which are least susceptible to the influence of atmospheric oxygen, and consequently have the smallest tendency to form fatty acids,

because these acids attack the metal and form with it compounds of a rusty-brown colour. Though tallow is often used for greasing ironware, it is one that very soon becomes converted into a rusty-brown mass, and allows the iron to rust. Liquid fats (oils, *e.g.*, olive oil) exhibit a still greater tendency to form rust, though this inconvenience may be minimised by boiling the oil for a short time with anhydrous sodium carbonate, whereby a slightly alkaline reaction is produced. A better result than that obtainable with vegetable oils can be ensured by using mineral oils, either alone or in combination with ozokerite (ceresin), or vaseline, the best of these, however, being wax and paraffin dissolved in benzine or turpentine. Wax and paraffin being neutral substances, exhibiting no acid reaction, therefore cannot give rise to the formation of rust on iron.

#### *Preventing Rust by Coating with Oxides.*

The formation of oxidised coatings on iron is an old-established practice, which includes the process of "browning"; nevertheless the method has never produced any noteworthy results, since the protection afforded is generally by no means permanent, and is suitable only for small articles, on which it can be frequently renewed, whilst for larger articles the tedious and expensive nature of the operation precludes its employment. For the sake of completeness, however, a few of the methods used are described.

#### *Bronze-coloured Oxide Coating for Iron.*

All the known methods of bronzing or browning iron by painting with acid solutions of copper or iron, drying the same in the air, brushing off the rust thus formed, and repeating the operation, produce simply a light or dark red-brown coating on the surface of the metal. Even the Barff method, in which the iron articles are heated in

superheated steam, are merely capable of forming a black film of oxide on the iron. Moreover, the two last-named methods present the disadvantage that the film of oxide soon peels off, thus affording an opportunity for the formation of rust. Again, though iron goods can be coated with copper or brass by dipping in solutions of copper, etc., or by galvanic methods, the coverings peel off after a short exposure to moist air, particularly if the surface of the iron was not perfectly bright to begin with. With the process now to be described, however, iron goods, especially for artistic purposes, can be easily coated with a fine, bronze-coloured film of oxide. This will resist the influence of moisture in a fairly satisfactory manner, and, moreover, the production of any desired shade of bronze can be effected by simple means. With this object the articles, scoured bright and freed from grease, are exposed for two to five minutes to the fumes of a heated mixture (1:1) of concentrated hydrochloric and nitric acids, the heating being continued until the bronze colour is visible on the surface of the goods. Then, after rubbing them over with vaseline, they are heated again until the vaseline begins to decompose, whereupon they are cooled and rubbed over with vaseline a second time. The fumes of these two acids produce a light reddish-brown shade of bronze, but when acetic acid is included in the mixture, the coating of oxide formed on the iron is of a handsome bronze-yellow colour; and all varieties of tone, from dark to light reddish-brown, and from dark yellow-brown to light bronze-yellow, can be produced by modifying the composition of the acid mixture. Iron T-rods, five feet long, for iron coffers, coated with a layer of oxide in this manner, have been found entirely unaffected at the end of ten months, although continuously exposed to the acid fumes impregnating the atmosphere of the laboratory.

*Ward's Inoxidation Method.*

This method of preserving iron from rusting is based on the conjoint application of silicates and heat. The articles of cast or wrought iron are coated with a siliceous material by brushing or dipping; the coating dries rapidly, and on being exposed to a suitable degree of heat becomes liquefied, is said to "soak into the pores of the metal" and when cold forms a dense and uniform dull black covering, which does not alter on prolonged exposure to the atmosphere, neither does it become loose, or peel off. The addition of vitreous pigments to the siliceous material produces very handsome decorative effects far surpassing those obtainable by painting in the ordinary manner.

*Thierault's Process.*

Thierault has invented a process for colouring iron and steel, which is intended to protect these materials from rust and at the same time improve their appearance: the method is widely used and has proved itself efficient.

The following mixtures are given in the inventor's Patent Specification as suitable for use in the process: Liquid No. 1 contains mercuric chloride and sal ammoniac; No. 2 consists of ferric chloride, cupric sulphate, nitric acid, alcohol and water; No. 3 contains ferrous chloride associated with nitric acid and water; and No. 4 is a weak solution of potassium sulphide. The articles, previously cleaned thoroughly and freed from grease, are given two coatings of liquid No. 1 by the aid of a sponge slightly moistened therewith, the second coating not being applied until the crust of oxide produced on the metal has been thoroughly dried, scrubbed over with black oxide of iron and a brush, and dried with a linen cloth. The same procedure is adopted in the subsequent treatment. Several coatings of No. 2 liquid are given and then liquid No. 3 is applied, the sponge being

in this case thoroughly soaked in solution. After drying for ten minutes the articles are transferred to a bath of hot water at  $90^{\circ}$  to  $100^{\circ}$  C., where they are left for five or ten minutes according to their size. When taken out again and dried they are coated several times with preparation No. 3, followed by a coating of No. 4 and by re-immersion in hot water. They are next rinsed and treated several times more with liquid No. 3 applied by means of carded cotton wool, the liquid being progressively diluted with water. A little olive oil is then brushed over the goods, which are afterwards rinsed, placed in hot water ( $60^{\circ}$  C.), and on removal rubbed well with woollen cloth, a little olive oil being used towards the last. Wrought or cast-iron goods treated in this manner present a handsome black, glossy appearance, especially when they have been finely polished.

#### *Inoxidation Process for Cast Iron.*

The cast-iron articles such as gasaliers, water pipes, ornamental pieces, balcony railings, saucepans and the like are laid on an iron slide about twelve feet long and heated to about  $600^{\circ}$  to  $700^{\circ}$  C. in a special furnace, an oxidising flame from a gas generator being employed for the first fifteen minutes, followed by a reducing flame for twenty minutes. When taken out and cooled the articles will exhibit a uniform slate-blue appearance and may be easily enamelled and decorated in any convenient way. When enamel is employed the usual pickling with acid is dispensed with, the enamel consequently adhering excellently. Many articles treated by this method have been exposed to the atmosphere out of doors for a couple of years without the slightest trace of rust being formed. It has been proved by numerous experiments that the tensile strength of iron is but slightly reduced by this inoxidation treatment, and in fact not more than usually results from heating to redness. With regard to the

durability of the superficial layer under a high load, it has been ascertained that in the case of wrought iron chipping-off first occurs at an average tension of about two tons (2012 kilos.), whilst in cast iron it does not loosen even under a breaking load.

*Iron Glaze ("Email de fer contre oxyde").*

This coating has been recommended as a cheap method of protecting iron pipes from the influences to which they are subjected when laid underground. The glaze is compounded of 130 parts of powdered crystal glass, 205 parts of soda and 12 parts of boric acid. These ingredients are carefully mixed and fused in crucibles, then quenched in water, pounded and ground to a very soft powder. The pipes or other iron articles to be glazed are first cleaned in the usual manner by pickling, then dried and covered with a very thin layer of gum-arabic (or other agglutinant), over which the pulverised glaze is afterwards strewn. After driving out all moisture by heating the articles to about 160° C. the temperature is raised to a dull red heat, which fuses the glaze. When the coating is uniform it adheres very strongly to the surface of the iron and resists all external influences. It is therefore particularly suitable for iron pipes that are required to possess special powers of resistance to external influences, but is too expensive for general use.

*Honigsmann's Ferrous Oxide Method.*

To prepare a metallic surface the iron articles are first dipped in a bath of boiling caustic soda (b.p. 140° C.), and then immersed in a second bath containing caustic soda supersaturated with iron oxide (either rust or the precipitated oxide).



*De Meritens' Anti-corrosive*

The process consists in immersing the goods in a bath of ordinary or distilled water heated to  $70^{\circ}$  to  $80^{\circ}$  C, where they are exposed to an electric current for one to two hours, whereby, through the action of the liberated oxygen, the surface of the metal becomes coated with iron proto-peroxide, which resists the action of the air and protects the underlying metal. The hydrogen collects at the other pole, i.e., the sides of the vessel, or plates of carbon or metal suspended thereon. The current should not be stronger than is necessary to decompose the water. The coating may be polished with clean brushes. For the treatment of steel, ordinary service water will suffice; but with wrought or cast-iron articles the inventor's attempts were unsuccessful until he employed distilled water and allowed the current to act for a while with alternated poles.

*Potassium Bichromate as an Anti-corrosive.*

This salt is said to be a useful means of preserving iron from rusting. The metal is painted over with a concentrated solution, and the articles when dry are heated for a couple of minutes in a stove or over a wood charcoal fire, whereby chromic acid is reduced. Heating must be continued until no yellow coloration is observed in the water employed in rinsing the goods. The requisite degree of heat is ascertained by a preliminary experiment; the employment of high temperatures results in the production of a glossy black coating. A similar coating can also be obtained by proceeding in the above-described manner, but using in place of potassium bichromate a solution of 1 part of sal ammoniac and 20 parts of ferrous sulphate in 60 parts of water.

*Method of Hardening Steel and Preventing Rust*

The finished and cleaned articles are heated to incipient redness, and, whilst in this condition, strewn with finely powdered caustic potash, whereupon they are reheated to the same degree, cooled in water, and rubbed dry with a woollen rag. Being now finished they must neither be ground nor polished. The only difficulty is in selecting the right degree of heat to apply, in order to keep the metal from being overhardened. On the other hand, the advantages of the method are: the hardened surfaces offer very prolonged resistance to rust, whilst at the same time the handsome uniform light grey colour is relieving to the eye, and imparts to the articles an appearance of greater strength and sturdiness than is the case with polished tools.

*Hanamán, Charlottenberg* (Ger. Pat. 281,803). Iron and steel articles are covered with an anti-corrosive coating by heating them by means of an electric current in an atmosphere of ammonia, etc., capable of forming a nitride, or in a solution of a nitrite forming fluid from such a gas.

*British Patents for Anti-corrosive and Anti-fouling Paints*

The list of British Patents for compositions to be used as preservatives for iron and as anti-fouling paints is a long one; we shall therefore content ourselves with a short list of the most important ones and those which appear to be of most value.

*Anti-corrosive Compositions.*

1854.

No. 1947. *Joseph Westwood and Robert Butler*. Iron ships or vessels are first coated with black varnish and then with a layer of asphalt or a coating of boiled oil and black lead or black varnish, asphalt and spirits of naphtha.

No. 442 *William Ryder and James Ryder*.—The composition for coating metals is made by dissolving 2 lb. of gutta-percha and 4 lb. of common rosin, tar, or pitch, and 1 oz. of gum shellac by heating to 160° F. with 4 gals of coal naphtha. Asphaltum may be used in place of rosin or pitch, and oils from bituminous schists in place of coal naphtha.

1855.

No. 4. *George Gram and John Jackson Crane*.—A composition containing white lead, red lead, litharge, japanner's gold size, boiled linseed oil, and turpentine is used for the purpose of protecting ships' bottoms from the action of sea water, also for preventing the adhesion of animal and vegetable matter.

No. 2931. *James Edgar Cook*.—The composition for protecting iron, etc.; is composed of shellac dissolved in methylated spirit or wood spirit.

1857.

No. 1839. *Edouard Beckmann Olofson*.—An improvement in the manufacture of pigments or colours for preserving iron; the composition named by the patentee "minium grey" or "diamond colour" consists of graphite, linseed oil, white marble or calx and sometimes a small quantity of sulphur.

1858.

No. 1377. *William Blizzard*.—Amongst a number of claims the patentee proposes to use a solution of india-rubber or gutta-percha combined with resinous or spirit gums for coating iron, etc.

1864.

No. 928. *John Campbell Evans and John Calvin Thompson*.—The material used by the patentees consists of finely divided copper or zinc mixed with a suitable proportion of drying oils, varnishes, bituminous or other adhesive compounds capable of withstanding sea water.

No. 1804. *Henry Edward Francis De Brion*.—The composition proposed by the patentees consists of vulcanised india-rubber 750 parts and mineral pitch 250 parts, melted together.

No. 3164. *De Brion*.—A composition for protecting metals is composed of gum benzoin 45 oz. and alcohol or methylated spirit 1 gall

1885.

No. 15,231. *J. Blenkinsop*.—A paint consisting of rosin, naphtha, pine varnish, and boiled linseed oil together with zinc dust and zinc oxide is employed for preventing galvanic action.

1890.

No. 1821. *C. B. Phillips and H. R. Lewis*.—The invention consists in applying a coat of lead or anti-fouling paint and, after drying, powdered copper is put on and well rubbed in, or it can be mixed with the paint

1896.

No. 25,675. *A. C. Furse*.—Finely powdered aluminum metal is mixed with a suitable medium such as liquid celluloid or shellac varnish.

#### ANTI-FOULING PAINTS.

Anti-fouling paints depend largely for their value upon the presence of poisonous products which are slightly soluble in water, and therefore dissolve slowly or are capable of being injected or absorbed by marine organisms with fatal effects.

1852.

No. 855. *Robert Mortimer Glover*.—Claim is made for the use of arsenite or arseniate of lead with or without the addition of red or yellow "sulphurets" of arsenic. Arsenite of copper is also added

1854.

No. 253. *Albert Robinson*.—The composition consists of

black lead or plumbago, together with gums, fatty, resinous, or waxy matters, gutta-percha, caoutchouc, or other medium, and to prevent the adherence of marine animals and plants to this polished surface poisonous materials such as oxides and "sulphurets" of arsenic, oxides of the same in combination with the oxides of lead and copper, or these latter oxides alone, carbonate of baryta, oil of *Croton tiglium*, or other suitable poison.

1856.

No. 2359. *Peter Ward*.—The invention relates to a composition consisting of an insoluble soap, of lime or other base, mixed with oxide of copper or other metallic oxide or compound.

1857.

No. 1481. *James Edgar Cook*.—This invention relates to the preparation of a poisonous compound made with wood spirit or methylated spirit, shellac, strychnine or atropia, and dragon's blood.

1858.

No. 298. *John Coutts*.—The pigment is applied in a heated state to the hulls of vessels and consists of carbonate of baryta, litharge, arsenious acid, asphaltum, oxide of calcium (lime), and creosote or oil of tar. Other materials, as for instance, bichloride of mercury, silicic acid, with caustic alkali, red oxide of antimony, gutta-percha, with benzole, camphine, or spirits of turpentine may also be used in place of some of the above or in conjunction with them.

No. 781. *Daniel McCrae*.—The claim is for a combination consisting of bone grease and sulphate of copper or other poisonous material.

1859.

No. 425. *Matthew Crawford*.—An improved metallic varnish is prepared by mixing plumbago or black lead, or gum varnish, arsenic, and spirits of wine.

1862.

No. 72. *Robert Johnson*.—The improved composition consists of mercurial or blue ointment, arsenic, and black lead in combination with drying oil, oil paint, or common coal tar or black varnish.

No. 1466. *Jean Pierre Jouvin*.—The patentee states that "trimercuric sulphate ( $\text{SO}_3 \cdot 3\text{HgO}$ ) mixed with Prussian blue ( $3 \text{FeCy} + 2\text{FeCy}_3$ ) produces by its contact with the alkaline chlorides of sea water one of the most violent poisons known to mineral chemistry, *videlicet*, the mercuric cyanide ( $\text{HgCy}$ ) in the shape of chloro-cyanide of mercury and sodium" The composition consists of 55 parts of turbith mineral with 45 parts of Prussian blue forming a homogeneous green powder. This is ground with 250 parts boiled linseed oil, 650 to 660 parts of red lead or other colouring matter equally good, and the above green powder 90 to 100 parts.

1864.

No 1652. *William Bolivae Davis*.—The composition consists of residuum of palm oil or tallow, carbonate of copper, arsenic, spirits of turpentine, benzine, or equivalent substance, and linseed oil, the proportions being given.

No. 1941. *Francis Cruikshank*.—The composition consists of mercurial compounds, *e.g.*, red oxide of mercury, white precipitate of mercury, oxychloride of mercury. These are combined with a solution of rosin and gutta-percha in turpentine.

1865.

No. 624. *Francis Cruikshank*.—The claim is for the use of cyanide of mercury.

1866.

No. 394. *Henry Edward Francis De Brion*.—The specification claims among other things the use of a material as an anti-fouling composition consisting of chloride of cyanogen,

to which is added cyanide of mercury and ferro-cyanide of copper, combined with vulcanised rubber dissolved in carbon bisulphide.

1878.

No. 2846. *H. A. Harvey*.—The claim is made for the use of arsenical iron pyrites, mixed with oxide of iron, or oxide of zinc, ochre or other colouring matter, and ground to a paint with linseed or other oil, and litharge or other drier.

No. 5088. *J. B. Hannay*.—The anti-fouling composition contains alcohol, shellac, resin, hard and soft gallipot, arsenite of copper, arsenite of mercury, basic chromate of mercury, and colouring matter.

1883.

No. 3320. *A. M. Clark*.—The patent consists in adding sulphocyanide of copper and arseniate of mercury to any ship's paint, tar, or varnish.

1886.

No. 7497. *J. Cameron*.—Carbolates or sulphocarbolates of metals, *e.g.*, mercury, iron, copper, or zinc are added to ordinary paints.

1892.

No. 12,732. *L. Pflug*.—Hydrazine, hydroxylamine, or their salts, or other substances which will act destructively upon protoplasmic organisms are employed.

1895.

No. 17,871. *W. L. Gunn*.—The composition is composed of one or more of the cresylates of lead, mercury, copper, iron, or zinc, mixed with suitable diluents.

1898.

No. 2553. *S. Warner and C. F. W. Perry*.—The composition contains copper oxychloride, iron oxide, red lead, white arsenic, kauri or other suitable gum, shellac, boiled linseed oil, resin, coal-tar naphtha, wood naphtha, and turpentine.

1904.

No. 24,733. *G. G. Schobert*.—The composition is made by melting resin or asphalt with shellac, and adding zinc oxide previously ground in linseed oil; benzoline, methylated spirit, or solvent naphtha, is then added followed by calcium arsenite ground to a paste in linseed oil and the composition is heated for two days.



## CHAPTER IX.

### TESTING PAINTS.

IN order to gain a closer insight into the influence of electricity on paint, a number of iron plates were coated with various paints, one portion of the plates being thoroughly cleaned, whilst another portion was artificially rusted, before applying the paint.

These plates were then suspended, under perfectly identical conditions, in accumulator boxes, and a strong current of electricity was passed through them, the surrounding water being in the one case strongly acidified with hydrochloric acid, and receiving in the other an addition of sal ammoniac. The results of these experiments were of a very surprising character, inducing Simon, who performed them, to prepare a paint, the pigment of which—electropositive towards iron—is capable of conducting both electricity and heat.

In the preparation of this paint Simon was influenced by the idea "that the arrangement of a small number of metallic conductors through the insulating layer of varnish to the iron will facilitate an outward flow of the electricity, whereby all destructive influences will be removed from the insulating and anti-corrosive varnish layer". In this view he was following the theory of Melsens with regard to the effect of lightning conductors not only to exert a protective influence, but also prevent spontaneous discharges. At the same time Simon succeeded in reducing the coefficient of radiation of the paint—which factor is 7·74 in the case of pure oil varnish, ranging from 5·0 to 4·40 for lead paints—to as

low as 0.60, by suitably modifying the composition of the pigment. This is a matter of some moment, especially for gasometers, large iron structures, boilers, steam-pipes, and vacuum apparatus. For instance the condensation of steam on a coating of Simon's conducting paint is about 80 per cent. less than on paints consisting of red lead and white lead. The increased conductive property was readily discernible on iron plates coated with this paint, when one of a pair of such plates was inserted in a closed circuit of two strong cells and the other joined up to a galvanometer, the passage of a current being indicated by the latter instrument in a very short time. The experiment succeeded equally well whether the plates were surrounded by dry air, excluded from air, or suspended in water containing hydrochloric acid or sal ammoniac.

Quite recently H. Loesner devoted attention to the testing of oil paints, and expressed himself on the subject as follows: "Just as in the testing of building materials the greatest value is placed on tensile strength, resistance to compression, etc., and the chemical constitution is rather of merely theoretical interest, so in the case of paints for iron-work the chief stress should be laid upon impermeability towards water and gases. Since, according to Simon, every paint is more or less porous, the first condition to be exacted of a good oil paint is that, when dry, instead of forming a porous layer it shall be perfectly homogeneous. When plates of sheet iron are coated with paint, rust forms—as is well known—on the surface of the metal after a short time. Owing, however, to the slowness of the reaction, immersion in water does not afford a suitable means for determining the durability of paint, whereas, on the other hand, steam places a very convenient method at our disposal for this purpose. With this object, plates of sheet iron are cleaned perfectly bright on one side, by means of emery paper, the

clean surfaces—which must not on any account be touched with the fingers—being then coated over with a thin uniform layer of the paint to be tested, and left to dry at the ordinary temperature for four days. The plates are next set, painted side downwards, over a boiling water-bath, so that the surface of the paint is just 2 inches (5 cm) above the constant level of the water. At the end of fifteen hours the plates are dried for a short time at 100° C. (not higher) and the layers of paint impregnated with aniline applied with a soft brush. Being thus softened they can be removed and the metal is then dried by means of alcohol. For the paint to be classed as good, the metal must have remained perfectly intact, a condition readily recognised by the appearance of the scratches formed on the surface by the emery paper used in the initial cleaning. Many paints will stand this steam test after the painted iron has been heated to 100° to 105° C. for about five hours.” Instigated by this report the author made several experiments on the action of steam on paints, and found that a two-months-old layer of red lead paint became somewhat soft, but otherwise remained perfectly intact, no trace of rusting being detectable. Under the influence of steam, a coating of lacquer paint softened and underwent partial contraction, without, however, laying the metal bare. Furthermore, fresh (two days old) layers of oil paint on iron withstood boiling in water for several hours without becoming loosened or otherwise suffering damage; whereas, on the other hand, in the case of a simple coat of varnish, a very short exposure—about fifteen minutes—to the action of steam sufficed to entirely counteract the adhesion of the varnish to the metal, the former being then removable by merely wiping it with the finger. For the present an expression of opinion on this method will be reserved pending the results of a contemplated series of experiments on the matter, and the author will content him-

self with remarking that anti-corrosive paints are designed for the protection of iron from atmospheric influences and not from the action of steam.

With regard to the formation of rust under paint on iron, Simon has latterly issued the subjoined report. He says: "The doubts previously aroused in my mind as to the inaccuracy of the general assumption that rust on iron is the result of fine hair-like cracks in the paint have been converted into certainty by the peculiar phenomena noticed in the course of my studies on the action of sea water on iron plates coated with various paints.

"Accurately fitting iron plates were placed side by side in accumulator boxes and subjected to the action of sea water, in which they were immersed to the extent of two-thirds their entire area. Old plates—irrespective of the kind of paint with which they were coated—which had been exposed to the influence of sea water for six months<sup>1</sup> exhibited, for a distance of several centimetres above the water line, cracks, blisters, and peeling off on the part of the paint, according as it contained a larger or smaller proportion of varnish. That part of the plates which was under water seemed, to a superficial observer, to be unaltered, save for rust spots, except that the white lead paint showed a readily recognisable amount of destruction and far-reaching decomposition. In the other plates the paint, so far as the part under water was concerned, still appeared to be coherent, though soft and—when dried—dull and somewhat rough. For about 1½ inch (3 to 4 cm.) above the water a distinct alteration in form was noticeable, the paint being blistered, peeled off, and loosened. This alteration and mechanical destruction of the layer of paint progresses outwards from the interior, as may easily be

<sup>1</sup> A series of parallel experiments with fresh water failed to yield any available results, owing to the development of a transparent mucus of mould fungi which, in a short time, produced a visibly destructive effect on the paint

gathered from an inspection of the various plates. The paint has allowed the sea water to gain access, thus reducing the adhesion between the paint and the metal, resulting in the occurrence of capillary attraction in the interstitial space, the effect being favoured by the evaporation going on above the water line. Furthermore, evaporation from the interior outwards results in the deposition of saline matter under the paint, which circumstance will naturally go hand in hand with the detaching of the latter. This phenomenon was noticed consistently throughout, irrespective of the kind of oil paint used, making its appearance in every repetition of the experiment; in fact the results entirely bore out and confirmed my previously expressed opinion that paint behaves exactly like animal epidermis in being, in its distended state, permeable by gases and liquids."

Further investigations were made by Simon on prepared coats of paint laid upon a substratum of glue, afterwards loosening them by simple immersion in water thereby obtaining films of paint that had not been exposed to any chemical or strong physical influences. The films were supple, pliant, and elastic, and did not part with these properties when exposed to dry or moist heat. Simon says, further: "The permeability of the paint films was tested by stretching them over a glass beaker half filled with hot water. When the film assumed a concave form as the water cooled, this afforded evidence of impermeability and the absence of any disruption. On pouring water tinged with aniline dye into the concavity before the water in the beaker had thoroughly cooled, fine drops could be observed to collect on the under side of the film, and these increased in size, while the water in the cavity diminished in volume. The same films were spread over a small dialyser and tested for permeability to variously coloured waters under normal atmospheric pressure, with or without an addition of brine. Whilst during the first twenty-

four hours no visible transfusion of the water through the film of paint could be noticed, a rapidly increasing interchange developed after the lapse of that time, and this was still more apparent when brine was employed as the diffusive liquid. The results were similar throughout a number of experiments performed with various films of paint under different conditions, and the penetrability of the films by air, illuminating gas, and sulphur dioxide was also demonstrated." Simon also made further observations in the softening of paint by dew on the ironwork of bridges and by water of condensation in stables, the result being the formation of rust; and he expressed the opinion that "rusting is not attributable to the iron having been insufficiently cleaned before painting, but rather to the deposition of dew, the result of rapid cooling of the metal, the liquid being then absorbed by the paint and brought into contact with the iron, which is thereby rusted".

In discussing Simon's experiments, the author would point out that exposure to sea water for six months is hardly the way to test the durability of paints intended for coating iron exposed to the air; and he would remark that the number of coats of paint applied should also be stated. The conditions being apparently unsuitable to the object in view, the results may be neglected and attention chiefly devoted to the permeability of the paint film. There can be no doubt at all but that a coat, or film, of paint will behave quite differently when in position on a solid substratum to what it does when loosened therefrom; and that it is altogether a different thing when a film of paint is stretched over a space containing air in a state of partial (though but slight) rarefaction. A cloak of waterproof material may be quite impervious to water when simply in a suspended position, whereas when stretched out so as to allow an accumulation of water to gather in the hollow thus formed it may probably allow some of the liquid to pass through. In the case of paint, the fatty substance of

itself repels water, which is thereby prevented from exerting continuous action, and hence penetration is considerably hindered. In fact, the author maintains that penetration of the paint is quite impossible, provided the work of painting has been done thoroughly and well, and he believes that such can then only ensue when the cohesion of the paint has suffered injury through the prolonged influence of atmospheric agencies. Penetration may perhaps be possible when the painting has been restricted to one or two coats; Simon states "that the anti-corrosive action of a paint increases in proportion to the quantity of linseed varnish it contains, and with the degree of insusceptibility of the pigment to chemical influences". This fact has already been recognised and emphasised by the author on previous occasions, as well as in the present work.

Having now seen how manifold are the influences capable of contributing towards injuring a coating of paint, we may next turn to the question of the length of time that a good coat of oil paint should last, and of the signs whereby incipient damage may be detected.

The durability of paint is so dependent upon its quality on local circumstances, that no definite period can be laid down. We have become acquainted with the influences that exert injurious action on paint, and it naturally follows that wherever they are present to an increased extent the life of the paint will be shortened, and *vice versa*. For instance, when continuously subjected to smoke fumes, acid gases, alkalis, etc., the paint will be ruined much sooner than where a purer atmosphere prevails; also when paint is exposed to the continued action of running or stagnant water it will be much less durable than in dry air. In districts where high winds, accompanied by much sand, prevail the paint will undergo mechanical attrition, which will largely contribute to its destruction. Under normal conditions it may be

assumed that a good coat of oil paint will last for five years, or for even as long as eight years under specially favourable circumstances, before requiring renewal.

The signs by which one can recognise that a paint has ceased to discharge its protective functions have already been touched upon, namely the alterations in outward appearance, and the occurrence of rust spots in the paint itself.

If the paint exhibits cracks, be they ever so fine, or if it has become dull and crumbling so that the pigment can be wiped off in the form of powder by the hand or with a cloth, the admission of moisture will have become possible, either directly through the cracks, or by absorption and retention in the paint, and the iron will necessarily begin to rust. In such events repainting is an urgent necessity. Rusted places show themselves in the paint, at first by the appearance of yellowish-red patches, sometimes spread over the entire surface of the iron structure, at others only at the rivets and screws. No actual rust may be visible as yet, but it appears as though the moisture had drawn the rust by capillarity through the absorbent paint; only at a later period does the paint disappear more and more, whilst rust patches and incrustations become apparent; it then becomes high time to renew the coat of paint, carrying out this operation with as much care as if the structure were entirely new.

#### METHODS AND APPLIANCES FOR TESTING THE UTILITY OF ANTI-CORROSIVE PAINTS

*(Specification of the Swiss Institute for Testing the Strength of Materials.)*

1. *Determination of Colour.*—The shade of colour is examined after the laying on and drying of the paint.

2. *Chemical Composition.*—All that is required under this head is to ascertain the constituents of the paint: *viz.*, the pigment, vehicle, and any driers present. The quantitative



examination of the pigment does not come within the scope of the work, but on the other hand the resistance to acids is determined, 2 per cent. hydrochloric acid or 2 per cent. sulphuric acid being used. Ten grams of the pigmentary matter of a paint, washed clean with carbon bi-sulphide, ether, alcohol, or water, are covered by 100 c.c. of the dilute acid for three days, with occasional stirring, then filtered, and the total weight and qualitative composition of the dissolved matter determined.

3. *Alteration of Weight in Drying.*—To obtain information on this head equal weights of the paints are freely exposed in large basins to the air for seventy-two hours in succession at constant temperatures of 50° and 100° C. respectively.

4. *Amount of Paint used in Painting a given Area.*—To ascertain this factor and the consequent relative cost of painting with different paints, cleaned and weighed plates of black and white metal 1 foot square are carefully painted with two coats, and weighed three days after each painting. The mean difference in weight obtained from six plates gives the average quantity of paint consumed, and from this the amount per square yard (or metre) can be calculated.

5. *Rate of Drying.*—Uniformly painted sheets of iron about 24 inches long by 12 inches wide are used. Notice is taken of the time at which a 9 × 1 inch strip of smooth writing paper, pressed evenly on the surface of the paint by the aid of a soft roller and immediately removed, ceases to show any stain. Furthermore, the time whereat the paint no longer sticks to the paper strip, or to the dry skin of the finger, is also noted.

6. *Adherence and Toughness of the Paint.*—Plates of black and white sheet iron and zinc, carefully cleaned, and painted without priming, were stored for three months in the physical laboratory of the institute, at a mean tempera-

ture of 16° C., and exposed to a uniform circulation of air. At the end of that time one half the plates were placed on end in a drying oven in such a manner as to allow the air to circulate between them, and were heated to a constant temperature of 50° C. for twenty-eight days. Each plate of both sets was then cut in two, and one half exposed fifty times to 16° to 23° (C.) of frost. Finally all were subjected to repeated folding tests, through 180°, until cracks were formed, steel bolts  $\frac{2}{8}$  inch in diameter being used.

7. *Covering Power and Resistance to Acids.*—The covering power was tested by covering the surface of iron sheets and basins, either with two coats of the sample of paint under examination, or with two coats over a priming of red lead or iron oxide. The basins, after being left to dry for three months, were filled with a 5 per cent. sulphuric acid, and examined for three days. In the case of acid-resisting paints of poor covering power the acid forces its way under the paint, liberates bubbles of hydrogen, and loosens the paint locally in patches at the bottom of the basin, without, however (in the generality of cases), destroying the constitution of the paint mass itself. Attempts to determine the covering power by photometry failed to yield any satisfactory results.

Perhaps the most complete series of tests which have been made as to the protective action of various paints are those carried out by the American Society for Testing Materials on the Havre de Grace Bridge on the Pennsylvanian Railway and on steel plates at Atlantic City. With regard to the former tests, panels on the bridge were painted with nineteen different compositions in 1906 and were examined from time to time by a committee specially appointed for that purpose who reported upon the condition of the various panels. The composition of the paints is given in the report, but it is sufficient here to state that none of them

were very successful, in most cases the results being poorer than with the ordinary paint used on the remainder of the structure. The steel plates exposed at Atlantic City were painted in 1910, and when they were examined it was found that the paints which afforded the greatest protection were in the following order:—

No. of Pigment.		Average Ratings				
		1910.	1911.	1912.	1913.	1914.
9	Orange mineral . . .	9.0	8.3	6.9	4.0	3.0
10	Red lead . . .	8.7	8.3	8.1	6.3	4.0
16	Natural graphite . . .	9.1	6.8	6.6	6.2	4.0
17	Artificial graphite . . .	7.1	5.9	4.4	2.0	0.0
34	American vermilion . . .	9.1	10.0	9.9	9.8	7.5
36	Medium chrome yellow . . .	7.0	7.7	6.0	5.2	3.5
39	Zinc chromate . . .	9.4	9.5	8.8	8.0	4.0
41	Chrome green . . .	9.8	9.8	8.6	7.6	5.0
49	Zinc and lead chromate . . .	9.5	9.7	9.2	8.3	4.0

The average ratings represent the opinion of each member of the committee as to the preservative action of the various pigments expressed in figures and averaged, total protection being taken as 10. The method is empirical, but it will serve in absence of a better method. The remarkable point about these tests is that American vermilion (*i.e.* basic lead chromate) shows a much higher preservative action than any other pigment, while iron oxide and Venetian red are so poor that they are near the bottom, being rated at 2.5 and 1.5 respectively.

L. P. Nemzek, chief chemist, John Lucas & Co., in an address presented at the thirteenth annual convention of the Maintenance of Way Master Painters' Association of the United States and Canada, held at Philadelphia in 1916, drew attention to the value of American vermilion as a preservative paint for iron and steel, and it is somewhat remarkable that it has been so long neglected. This may be due to its

high price, but it must be remembered that a paint made from it weighs only about half that of red lead paint, besides which it will spread somewhat further bulk for bulk, does not settle out on standing, and the paint has not such a great tendency to run when laid on vertical or inclined surfaces. As pointed out by the above author where economy is in question American vermilion can be mixed with say 25 per cent. of a chemically inert pigment such as "Asbestine" and yet be equal in covering and spreading power to a straight red-lead paint.

## CHAPTER X.

### OFFICIAL STANDARD SPECIFICATIONS FOR IRONWORK PAINTS IN VARIOUS COUNTRIES

RECOGNISING the importance attaching to the proper painting of iron structures, Provincial, Government, Railway, and Naval authorities, *inter alia*, in different countries prepared certain specifications relating to the paints supplied by their contractors. Whether these conditions really meet the requirements of the case is more than doubtful, since we find that one specification prescribes pickling with acid and painting with red lead, while another rejects these altogether, from which it is evident that no unanimity of opinion exists as to the usefulness or the reverse of these methods. In the same way, some enjoin the use of white lead or zinc white oil paint, whilst another prohibits them.

For the general information of the reader the author reproduces a series of requirements actually prescribed for paints to be used on iron structures, and supplements the list with specifications, which he believes worthy the serious attention of all parties interested in the matter.

In Austria a number of widely variable anti-corrosive paints are in use, both for priming and finishing coats for ironwork. The State and private Railway Companies, and the larger State and Local Authorities, have several specifications with which the bridge-building companies have to comply. In all cases where the use of white lead for priming is not expressly stipulated iron oxide is favoured, zinc white, toned as required, being employed for the finishing coats.

For the Imperial Royal Austrian State Railways the following conditions are prescribed.—

All bridges and lattice work, together with sills and fixing screws, shall receive a covering of oil paint, applied in three coatings, each of which must be thoroughly dry before the succeeding one is laid on. All painting in the open must be postponed until the occurrence of a continuous spell of warm, dry weather. The surfaces to be painted must first be freed from all rust, roughness, and impurities by scouring with wire brushes, and thorough drying. Surfaces that will be inaccessible when the structure is put together must have been previously covered with a single, durable first coat of red-lead paint, and this paint must also be used for the first coat of all the visible parts of the structure when put together. A stiff brush must be used for laying on the first coat, in order to ensure the penetration of the paint into all irregularities, joints, and cracks. When the bridge is mounted in position, the first coat must be carefully gone over, and made good before the second coat is applied, and the joints, etc., are to be then cemented with a putty made of red lead and linseed oil.

A thicker paint must be employed for the second and third coatings, the second being carefully gone over and repaired in all defective and weak places before applying the final coat, which latter must be darker in tone than the preceding one, in order that they may be readily distinguished. If the ironwork is not properly covered by these three coatings the contractor is liable to be called upon to apply a fourth free of charge.

Wherever the wooden sills or sleepers come in contact with the ironwork the latter must be painted a third time before the former are put in position.

There is also an additional clause prohibiting thick painting even where it is to last for seven or eight years and more.

on the ground that such paints form a tough, coherent skin which masks any underlying cracks or flaws in the material of the structure, thus preventing their detection by the inspectors.

The specifications of the Kaiser Ferdinands Nordbahn Railway (Vienna) prescribes:—

That all contact surfaces of parts of ironwork that are to be riveted together must have been first carefully cleaned from rust and dirt and painted with red lead.

Bridges and lattice work, with all sills and fixing screws, shall be painted with oil paint.

Every oil paint must be applied in four coats, none of which may be laid on until the preceding one is thoroughly dry.

Painting in the open air must be delayed until a continuous spell of warm, dry weather sets in.

The surfaces to be painted must be first carefully scoured with wire brushes to remove all rust, roughness, and impurities, and well dried.

Surfaces that will be inaccessible when the structure is put together must have been previously covered with a single, durable, first coat of red-lead paint, and this paint must also be used for all the visible parts of the structure when put together.

The first coat must consist of a thin easy-flowing paint, laid on with a stiff brush, so as to penetrate into all irregularities, joints, and cracks, and when the bridge has been mounted in position a second coat of red-lead paint must be applied.

When the first coat is thoroughly dry, cementing with a putty composed of red lead, or zinc grey, and linseed oil is proceeded with.

For the third and final coats a thicker paint, of pure white lead, is to be used, this being toned to grey by the

addition of a little black. Before painting with the final coat, the preceding one must be gone over carefully, and all deficiencies and weak places made good. To enable them to be distinguished, the fourth coat must be darker in colour than the third. Should the fourth coat afford insufficient covering to the structure, the contractor may be called upon to provide another coat of paint free of charge.

All parts of the ironwork that will come in contact with wooden sills or sleepers must have received a fourth coat of paint before the latter are put in position.

A special report with regard to paint for iron bridges, issued by the Building Department of the Municipality of Vienna, states :—

1. To preserve iron bridges either a twofold coating with platinum or silicate paint is required ; or else a paint made of chemically pure white lead, topping a first coat of red-lead paint. No other addition to the powdered dry metallic pigment than pure unadulterated linseed varnish should be permitted.

2. If tendered at equal prices the platinum or silicate paints should be accepted in preference to white-lead paint. A single first coating with red lead is a usual preliminary condition to painting with ordinary paints, but in the case of platinum or silicate paints is radically at variance with the nature of these paints, and should therefore be omitted.

In the special conditions laid down by the Provincial Government of Lower Austria with regard to the erection of the State road bridges over the Danube at Vienna the question of paint is dealt with as follows :—

The paint must consist of mineral pigments and linseed oil of best quality, finely and smoothly ground, and properly made ; red lead being used for the first coating, and the grey pigments, white lead or zinc white, with an addition of black or zinc dust, for the final coats.



The authorities of the Prussian State Railways prescribe the following conditions for paints in their special contract specifications for the supply of large mounted iron structures:—

As soon as the materials have been made ready, by trimming the edges, and making the rivet and screw holes, but before the parts are put together or painted, all the iron must be carefully cleaned from rust, dirt, dust, and scale, either by dry scouring with brushes, etc., or by pickling with dilute hydrochloric acid, etc., and at once coated with a layer of paint composed of hot linseed varnish with 10 per cent. of zinc white. If pickling has been performed, the adherent acid must be removed by dipping the parts in lime water, followed by rinsing in clean water and heating to 100° C. in boiling water. Then, after all the adherent water has evaporated, they must be provided with a thick coating of paint consisting of 90 per cent. of good thin, quick-drying linseed varnish, free from water or acid, and 10 per cent. of zinc white, and put away to dry in covered rooms.

After the operation of cleaning and painting, the goods must be offered to the officials for inspection.

Immediately before riveting, the parts to be joined must be cleaned at the contact surfaces, and then painted with red lead and attached so tightly together that they cannot move while being riveted. If any parts warp or distort in riveting, the connections must be loosened, and after the pieces have been officially inspected must be carefully put right, or replaced by new ones.

#### *Paint.*

1. *In the Workshops.*—Until officially inspected and tested the various separate or mounted parts of the structure may not be painted with anything more than linseed varnish paint. As soon as the inspection is over, the various pieces must be

carefully cleaned, the joints of contact surfaces cemented with a stiff putty made of white lead and linseed oil, and the whole painted with red-lead paint.

The first coat must be laid on thin and be allowed to dry thoroughly,

2. *When mounted*, all the defective parts of the paint applied in the workshops must be made good, and the places where rivets have been driven during mounting must be gone over. After cementing all the joints of contact surfaces the whole of the ironwork must receive another coat of pure red-lead paint, followed by at least two coats of good covering oil paint of the colour prescribed by the railway authorities. All interstitial spaces in which water is likely to accumulate must be properly cemented with asphalt putty and painted smoothly. In the case of galvanised parts the first coating of red-lead paint is omitted.

All surfaces coming in contact with earth, stone, sand, mortar or masonry must be coated with heated wood tar of good quality instead of with oil paint.

In Russia iron oxide is almost exclusively employed for the preliminary coating of iron structures, and, it is averred, with good results, though a few of the railways use red lead. White lead, suitably tinted, forms the principal covering paint, especially for bridges over railways.

At the present time a paint termed "Iron Protector" is being recommended for the preservation of iron against rusting. This preparation appears to be a kind of armour-scale ("Panzerschuppen") paint containing also earthy pigments.

The Government of the Netherlands prescribes the following conditions with regard to the painting of iron structures:—

The iron is dipped for twelve hours in a bath consisting of 15 per cent. hydrochloric acid diluted to 6° with water, after

which it is fished out with iron hooks or cranes, washed thoroughly with water by scrubbing and then worked about in a bath of lime water. After this it is swilled and freed from rust, to be next immersed in boiling water in a long pan, where it is kept until quite hot, and on removal after it becomes dry it is painted all over with a drying oil.

Following this treatment the metal is shaped and finally coated with two layers of minium—this can only mean lead minium (red lead), as the specification has been in force a long time. However, according to Kloes, iron oxide has now to a large extent replaced true minium for iron structures, the latter being only rarely met with on bridges, roofs, and similar structures.

The regulations laid down by the Eastern Railway of France (*Chemin de Fer de l'Est*) for the painting of ironwork are as follows:—

After being weighed all iron parts are to be cleaned with metal brushes and painted with minium, this coating being touched up after the parts are mounted in position.

The minium paint must consist solely of red lead ground with linseed oil and turpentine substance (essence or spirit is probably meant); the latter materials must be fresh. During the application of the first coating the railway officials will take samples of the materials and subject them to chemical examination. Should the red lead prove to contain more than 2 per cent of impurities, or extraneous admixtures be detected in the linseed oil or turpentine, the paint will be rejected and must be taken away and replaced by the contractor, even when the results of the analysis are not made known until after the ironwork has been set up in position.

The Italian Mediterranean Railway Company prescribes the following standards for iron paints:—

After the provisional acceptance and weighing of the iron

materials all the parts must be carefully cleaned from dirt and oxide, and painted with red lead mixed with pure boiled linseed oil to which 3 per cent. of litharge has been added.

No two pieces may be riveted together until the contact surfaces have been coated with the above paint. All the parts must be cleaned anew before and after mounting and the first coating of red-lead paint touched up, all the interstitial spaces at joints being filled up with minium. Thereupon two coats of white-lead paint, prepared in the same way as the preceding paint, must be laid on, the colouring matter for the same being determined by the railway authorities.

Each coat of paint must be allowed to dry thoroughly before the next one is applied, and care should be taken to carry on the work under favourable atmospheric conditions. Before laying on the first coat the surface of the iron must be well cleaned, scraped, and, if necessary, scoured with pumice stone. The white lead used must be pure, and therefore free from any admixture of lime, barytes, zinc white, etc.

Section 7 of the normal specifications, for the supply of ironwork for bridges and elevated structures, drawn up by the United Association of German Architects and Engineers, deals with—

*Cleaning and Painting.*—Before putting together, the various parts must be freed from all impurities, rust and scale, the method of cleaning to be stated by the contractors when tendering, except where any particular method is prescribed by the special conditions, or the contractor desires to deviate from the latter. If chemical means are resorted to for this cleaning, the contractor is liable for any subsequent rusting due to carelessness in removing the acid. The parts (plates, rods, etc.) chemically cleaned must be painted over with thin, quick-drying linseed varnish whilst hot, immediately after cleaning, and kept under cover until the

varnish is sufficiently dry. Before the covering paint is applied, notification must be given to the consumer so that he may first examine the ironwork; and it is only after the treatment necessitated by this preliminary acceptance of the goods, and repairing the defects in the coat of varnish, that the first coat of the particular paint stipulated in the contract may be laid on. All surfaces that are to be covered up by others must be painted before the parts are put together.

In the case of all interstitial spaces where water is liable to accumulate, the painting must be very carefully performed, and provision made for the draining away of the water through holes bored for the purpose. If the latter is impracticable, the spaces must be filled up as completely as possible with asphalt putty, or some other suitable material.

After the structure is mounted, the heads of all rivets put in during that operation must be freed from rust and primed, and all crevices filled up with putty. Unless specially mentioned in the contract, no other painting need be done.

The Italian Ministry of Public Works has laid down the following conditions regulating the taking over of iron railway bridges from the contractors:—

The contractor must not employ for the paint any materials that have been adulterated or do not comply with the terms of the contract. The pigments must be well ground on the stone, with an addition of linseed oil, the drying of which may be facilitated by an admixture of 3 per cent. of litharge to the hot oil. A further addition of linseed oil and turpentine, in equal parts, is then made to the paint.

The linseed oil must be well refined, clear, inodorous, and of bitter taste; and the white lead (lead carbonate) must not contain any admixture of lime or barytes.

*Painting the Metal.*

Parts of a structure should never be finally joined up without the contact surfaces having been properly painted with red-lead paint.

The first coating of red lead should be applied in the workshops, after the surfaces have been properly cleansed, scraped, and, if necessary, scoured with pumice, but not until the ironwork has been conditionally passed by the examining official. When the parts have reached the place where they are to be mounted, they must be carefully scraped clean of rust and dirt, especially those surfaces that are to come in contact with others, and the existing first coat of paint must be completely repaired.

The officials may order this first coating to be scraped off altogether, so that they may, on occasion, convince themselves of the quality of the material used in the structure. In such cases the said coat must be carefully renewed.

When the parts are mounted, a second coating with red lead must be applied on all the outer surfaces of the structure, not excluding those that cannot be seen from the outside.

In addition to these two coats, three others must be laid on after the structure is completed, white-lead paint being used along with the necessary toning pigments to produce the required shade.

When, in spite of all precautions, crevices are left between riveted parts, they must be filled up with red lead, after the first coat of white paint, to prevent the intrusion of moisture and consequent oxidation. Each coat of paint must be perfectly dry before the next one is applied. The officials are empowered to fix a period within which the last three coats must be put on.

On the Swiss Railways the following regulations exist for the cleaning and painting of iron structures:—

The surface of the iron must be cleaned by dry scouring with selected sharp fragments of coke, or pickling with dilute (10 per cent.) hydrochloric acid, followed by neutralising with milk of lime and rinsing clean with boiling water. The cleaned parts must then be immediately painted in the workshop with hot linseed oil and afterwards with white-lead paint. Surfaces that will be covered up by others must have a double coat of white-lead paint over the varnish.

No parts must be sent from the shops to destination until the entire surfaces have been carefully primed and the paint has thoroughly dried. After the erection of the structure all fresh rivet heads must be primed, and the first coating must be repaired or renewed wherever defective or injured.

Whether, and to what extent, any further painting is to be done by the contractor depends on the terms of the contract. In any case such work must not be commenced until the first coat is perfectly dry and permission has been given to proceed.

The Swiss North-Eastern Railway has recently discarded red-lead paint in favour of armour scale ("Panzerschuppen") paint or Bessemer paint. The following conditions are imposed:—

(a) *Varnish.*

1. Only well-stored, acid-free linseed oil may be used in making the varnish.

2. The density of the varnish must not be below 0.93.

3. When dissolved to an alcoholic soap solution the varnish must not exhibit a milky appearance on the addition of water, though opalescence is permissible.

4. When spread out on glass plates the varnish must dry within twenty-four hours.

*(b) Paint Mass.*

1. Colour: dark grey.
2. When laid on naked or primed iron the paint must be readily distributable, cover well, be tough and remain elastic, without peeling.
3. On being spread out thin the paint must dry within twenty-four hours.
4. The paint mass must be acid-proof, and free from any constituents liable to become soluble in water under the action of sulphuric acid or atmospheric carbon dioxide.
5. No action should be detectable after forty-eight hours' exposure to 5 per cent. sulphuric acid, the paint being applied as a double coat on an unprimed iron basin.

The following general conditions for painting on iron were drawn up by Joan du Kloes (architect) :—

All iron parts should, as soon as tested, be painted over with red-lead paint, the exposed portions receiving two coats, whilst for those forming the inner part of the structure one will suffice. The selection of the colour is a question for the customer.

Wherever possible the red-lead coating should be applied before any rust has formed, and in no case should the painting begin until all rust has been removed, either by scouring with sandstone or pickling by six to twelve hours' immersion in a bath of 6° Bé. hydrochloric acid; after scrubbing with stiff brushes, plunging in a bath of lime water, and swilling with boiling water, the iron is dried as quickly as possible and painted. The lime water ought to be renewed whenever traces of free acid are detected by test-paper. Du Kloes gives as his reasons for leaving the choice of cleaning methods open, that opinions are divided, and that he finds sometimes one plan is best, sometimes the other. For example, a rolled T-girder, when smooth, can be easily scoured with a bit of



sandstone, and in this case it is therefore advisable to merely scour and brush, since this plan saves the trouble and care attendant on the wet method. On the other hand, for girders made by riveting iron plates and angle-irons, mechanical cleaning is beset with difficulties, it being impossible to scour the rivet heads and adjacent surfaces sufficiently clean, and in such event, he thinks, pickling is indispensable. The painting of large iron articles before rust has had time to form, *i.e.*, whilst the surface of the iron still remains perfectly blue, is in reality seldom performed, and as a matter of fact would be useless, on account of the various operations of boring, blocking, straightening, and riveting, to which the parts have to be subjected. Provided pickling be carried out with care and with proper appliances, the method is less tedious than scouring. The removal of the rust is based less upon actual solution or dissociation than on the liberation of hydrogen; and the chief point is to ensure contact of the acid, lime water, and rinsing water with the whole of the rust particles. Furthermore, the scrubbing must be done vigorously and not merely in a perfunctory manner, and by this means, coupled with a good swilling with hot water, all residual traces of acid, lime water, dissolved rust, and any chloride of lime present must be got rid of. If the water is used very hot the iron will dry spontaneously on being taken out of the bath, and can then be painted immediately. This is the only reason for employing heat in the process.

The author has always limited himself to red-lead, and considers it advisable to adhere to this course for the first coating. In view of Mulder's researches, he would not offer the slightest objection to the substitution of such pulverulent bodies as iron oxide, powdered roofing tiles, and so forth in the preparation of the topping paint.

For the two first coats of paint white lead should not be used, because of the traces of acetic acid that are developed

when this pigment is boiled with linseed oil, and which are likely to prove injurious; but as an external covering there is no objection to white lead being used. Of course, in view of the shades of colour required, it is not always possible to use red-lead; and, similarly, it is not always feasible to confine the varnish to boiled linseed alone, because under certain circumstances raw oil must be employed. For example, the German Government specifications prescribe the use of raw and boiled linseed oil, half and half, for mixing with the pigmentary powder. Du Kloes does not assume this proportion to be always the most favourable one; in fact, he inclines to the view that boiled oil should predominate, raw oil being only added to make the paint work more easily and prevent it drying too quickly when exposed to a hot sun.

The author's propositions for carrying out the painting of ironwork are as follow:—

1. Iron should not be painted until perfectly free from rust, the method of cleaning—whether mechanically, by scouring with pumice, coke, or wire brushes; or chemically, by pickling—being dependent on the shape of the metallic object or parts. Wherever possible, pickling should be avoided; but, if the shape of the ironwork precludes other methods, then care should be taken to keep the alkaline bath used for neutralising the acid up to a proper degree of strength, and to thoroughly dry the metal by an increase in temperature after cleansing with water.

2. The iron must be perfectly dry before painting is begun; a rule to be observed at all stages of the operation.

3. The first coating for iron should consist of hot linseed varnish, very carefully applied, so that all parts are covered. On this coating of varnish, which will afford sufficient protection against rust, is applied a first coat of paint composed of pure red lead in good linseed varnish, after the parts of the structure have been put together, all contact surfaces,

bored holes, rivet heads and bolts having been painted beforehand.

4. Ground oil paints should alone be used, and these should be applied by the aid of suitable brushes, merely mixing up the pigment and varnish just before use, and without grinding, should not be permitted. Furthermore, the painting must be done by skilled workmen and not by day labourers.

5. After priming, three coats of paint should be laid on at intervals of not less than a week, it being essential that one coat of paint should be quite dry before the next one is applied.

6. After the first coating with red-lead paint all fissures, holes, flaws, etc., must be filled up with red lead and linseed oil putty, the subsequent painting being deferred till the putty has thoroughly hardened.

7. The paint must be easy working, cover well, be free from turpentine, benzine, or other hydrocarbon diluents, and of all liquid driers, and must dry rain-proof within twelve hours.

8. The constituents of the paint must fulfil the conditions of—(1) *Pigment*: inert and requiring a large proportion of linseed varnish to become workable; (2) *Varnish*: pure linseed varnish of good quality, free from extraneous admixtures.

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